

# **FEASIBILITY STUDY FOR THE DEVELOPMENT OF LOW TEMPERATURE CURING ADHESIVES**

by

**H.E. Green, J.D. Sutherland and C.H. Sheppard**

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ONE SPACE PARK • REDONDO BEACH • CALIFORNIA

prepared for

**NATIONAL AERONAUTICS AND SPACE ADMINISTRATION**

**NASA Langley Research Center**

**Contract NAS1-12309**

**Vernon L. Bell Jr., Project Manager**

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1. Report No. NASA CR-132422		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle  Feasibility Study for the Development of Low Temperature Curing Adhesives				5. Report Date May, 1974	
				6. Performing Organization Code	
7. Author(s) H. E. Green, J. D. Sutherland and C. H. Sheppard				8. Performing Organization Report No. 22743-6009-RU-00	
9. Performing Organization Name and Address  TRW Systems Group Redondo Beach, California 90278				10. Work Unit No.	
				11. Contract or Grant No. NAS1-12309	
				13. Type of Report and Period Covered Contractor Report	
12. Sponsoring Agency Name and Address  National Aeronautics and Space Administration Washington, D. C. 20546				14. Sponsoring Agency Code	
15. Supplementary Notes  Project Manager, Vernon L. Bell, Jr., NASA Langley Research Center					
16. Abstract  The feasibility of a new approach for the development of stable, easily handled, room temperature (293 K-311 K) curing adhesives was studied and demonstrated. The work concentrated on a family of unsaturated amide/ester resins. Twelve candidate resins were synthesized and tested for completeness of cure at room temperature, adhesion to aluminum and titanium, shear strength, moisture resistance and heat stability. The three most promising candidate resins were selected and recommended for further development.					
17. Key Words (Suggested by Author(s))  Adhesive Resins Low Temperature Cure Amide/Ester Resins Unsaturated Resins				18. Distribution Statement  Unclassified - Unlimited	
19. Security Classif. (of this report)  Unclassified		20. Security Classif. (of this page)  Unclassified		22. Price*  \$3.00	
				21. No. of Pages	

\* For sale by the National Technical Information Service, Springfield, Virginia 22151

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ALL INFORMATION CONTAINED  
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DATE 11/19/01 BY 60322 UCBAW

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## FOREWORD

This document constitutes the final report for the work performed by TRW Systems during the period from 16 May 1973 to 16 February 1974 under Contract NAS1-12309, "Feasibility Study for the Development of Low Temperature Curing Adhesives," sponsored by the National Aeronautics and Space Administration, Langley Research Center.

This work was conducted under the technical direction of Dr. Vernon L. Bell, Jr. of the Langley Research Center, Hampton, Virginia.

The Applied Chemistry Department of the Chemistry and Chemical Engineering Laboratory, Applied Technology Division was responsible for the work performed on this program. Dr. E. A. Burns, Manager, Applied Chemistry Department and Dr. R. J. Jones, Head, Polymer Research Section, provided overall program supervision. Dr. H. E. Green was Program Manager. Major technical contributions throughout the program were provided by Mr. J. D. Sutherland and Mr. C. H. Sheppard. Acknowledgment is made of the technical assistance provided during the program by the following Applied Chemistry Department personnel.

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SUMMARY

This final report describes the work performed by TRW Systems during the period from 16 May 1973 to 16 February 1974 under Contract NAS1-12309, "Feasibility Study for the Development of Low Temperature Curing Adhesives," sponsored by the National Aeronautics and Space Administration, Langley Research Center.

The objective of this program was to determine the feasibility of a new approach for the development of stable, easily handled adhesive formulations which cure at ambient room temperature (293 K-311 K/68°F-100°F). Such materials will satisfy an existing need for adhesive resins with the versatility for use in field repair and initial fabrication of high performance bonded structures under a variety of environmental conditions, and will avoid undesirable stress build-up caused by elevated temperature cures.

The program objective was accomplished in a nine month technical effort concentrating on a versatile new family of resins which incorporate amide and ester chemical groups to provide high adhesion to metal substrates, as well as reactive vinyl-type chemical groups which can be made to combine to form a hard, mechanically strong structure between the bonded parts. The adhesive resins have been designed to be liquids at room temperatures to avoid the need for using toxic or flammable solvents to apply them. The study was conducted according to four principal tasks: 1) synthesis of candidate resins, 2) curing studies, 3) screening studies and 4) detailed characterization studies.

During the first task, twelve candidate resins were prepared from three readily available, multifunctional amino-alcohols and the acid chloride derivatives of four simple, unsaturated carboxylic acids. After

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screening several conventional amide-ester synthetic methods, a procedure involving the interfacial reaction of an aqueous solution of an amine-alcohol, with a tetrahydrofuran solution of an acid chloride, was chosen as the standard preparative method. This method was found to offer the best balance of high yield, short reaction time and ease of product recovery.

The candidate resins were characterized for correct structure by infrared and nuclear magnetic resonance spectroscopy. They were found to be >95% pure and free of unreacted starting materials by thin layer chromatographic analysis. In all instances, the resins were moderately viscous liquids at room temperature.

The curing studies, undertaken during Task II, were directed toward defining the most satisfactory resin curing agents and cure conditions for each resin system to facilitate a preliminary ranking of the candidates during the screening studies (Task III).

The curing reactions were conducted for up to 48 hours on each resin in the presence of 1%, 3% and 5% (w/w) of each activator-catalyst system. The tests were performed by mixing the appropriate quantities of an activator-catalyst system with a weighed sample of a resin, dividing the mixture into three approximately equal portions and then placing the portions on a glass grid. If an experimental sample showed evidence of cure (solidification with little or no tack) after the designated reaction time, it was placed in a sufficient quantity of concentrated (36 N) sulfuric acid to produce a 0.5% (w/w) solution if it dissolved. A sample was considered to be cured if it retained its integrity after two hours at room temperature (293 K/68°F) in the sulfuric acid.

The results of the curing studies provided clear evidence of the greater reactivity of the six candidate resins derived from acrylic (A) and methacrylic acids (B) than the six from crotonic (C) and vinylacetic acids (D). The latter resins resisted room temperature cure by a number of curing agents representing a variety of chemical types and activities. By contrast, the A and B derived resins could be cured in less than 24 hours with conventional peroxide/activator cure systems such as methyl ethyl ketone peroxide/cobalt naphthanate (MEKP/CN) or N, N-dimethylaniline/benzoyl peroxide (DMA/BP). In view of the resistance

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to room temperature cure evidenced by the crotonic and vinylacetic acid derived resins, work on those materials was de-emphasized during the later portions of the program and experimental efforts were concentrated on the screening and detailed characterization of the other, more promising candidates.

The screening studies (Task III) employed aluminum/titanium bimetallic curvature measurement specimens to aid in a preliminary evaluation of the candidate resins in terms of cure completion, adherence and resin/metal interactions.

The test specimens were prepared by bonding the metal strips with the candidate resin. After a 24-hour ambient room temperature cure, the specimens were heated at 344 K (160°F) for 16 hrs. After the test specimen had cooled to ambient room temperature, it was examined for residual curvature, adhesion and mode of bond rupture when separated.

The bimetallic strips bonded with the six candidate A and B resins were free of residual curvature, indicating that no further cure occurred in the hot air oven. Separation of the strips resulted in bond failure that was principally cohesive in nature. There was no evidence of deleterious adhesive/metal interactions.

The final portion of the program, the Task IV detailed characterization studies, was designed to assess the adhesion, thermo-oxidative stability and moisture sensitivity of the candidate resins. The results of these studies were used to rank the resins and aid in the selection of the three most promising candidates.

To test the moisture sensitivity of the resins, they were used to bond pairs of aluminum strips, which were then immersed in boiling water for two hours. The test specimens were monitored for retention of adhesive bond integrity and for changes in weight. The results of these tests served to differentiate clearly between the moisture sensitivity of the acrylic and methacrylic resins in that all of the former remained intact and suffered weight losses of less than 0.1%, whereas all of the specimens bonded with the B resins separated during the immersion or suffered severe loss of bond strength.

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The acrylic acid derived resins also showed their superiority in lap-shear strength tests. All of the A resins had room temperature lap-shear strengths with aluminum adherends in excess of  $7.6 \times 10^6 \text{ N/m}^2$  (1100 psi), whereas the B resin bonded coupons failed at  $5.3 \times 10^6 \text{ N/m}^2$  (770 psi) or less. The generally superior performance of the A resins is probably due to greater adhesion to the aluminum substrates. That interpretation is supported by evidence for 90-100% adhesive failure for the B resins, whereas the principal failure mode for the A resin bonded coupons was cohesive. The results of the room temperature lap-shear strength tests are extremely encouraging in view of the early stage of development of this resin system. By contrast to lap-shear strengths as high as  $11.7 \times 10^6 \text{ N/m}^2$  (1700 psi) for these neat resins, lap shear strengths of neat, room temperature cured epoxy resins are generally less than  $6.9 \times 10^6 \text{ N/m}^2$  (1000 psi).

The results of the detailed characterization studies clearly identify the three resins employing acrylic acid acyl components as the most promising candidate resins for further development as fully formulated adhesives.

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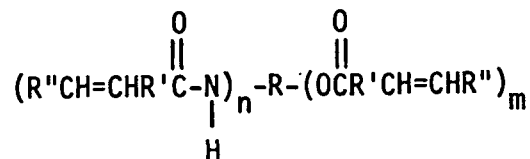
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## I. INTRODUCTION

This final report describes the work performed by TRW Systems during the period from 16 May 1973 to 16 February 1974 under Contract NAS1-12309, "Feasibility Study for the Development of Low Temperature Curing Adhesives," sponsored by the National Aeronautics and Space Administration, Langley Research Center.

The objective of this program has been to determine the feasibility of a new approach for the development of stable, easily handled adhesive resins which will cure at ambient room temperature (293 K-311 K/68°F-100°F). Such materials will satisfy an existing need for adhesive resins with the versatility for use in field repair and initial fabrication of high performance bonded structures under a variety of environmental conditions. The need for an improved adhesive system is a consequence of certain significant deficiencies of currently used materials. Of particular importance is the prolonged cure time (e.g., 4 hours) at elevated temperatures (often >340 K) required for full property development of state of the art high performance adhesive bonding systems. These stringent processing conditions render them unsuitable for use in field repair. Another significant problem associated with adhesives cured at elevated temperatures, arises from the introduction of undesired residual stresses when the part is cooled to room temperature or below. TRW's approach to provide the required improved room temperature curing resins concentrated on a new family of multifunctional, unsaturated amide/esters having the general structure shown below:



Where R = an aliphatic, or cycloaliphatic moiety; R' may be absent, or if present may be a moiety the same or different than R; R'' = H or a moiety the same or different than R or R'; m = 0 to 3, n = 0 to 3 and m + n must total 3 or greater. This basic structure, conceived and reduced to practice under a TRW Internal Research and Development effort, was designed to provide for a high degree of control of physical, chemical and mechanical properties through variation of its molecular components and choice of catalyst, in addition to the usual techniques of adhesive formulary.

The nine-month technical program to prove the feasibility of this new adhesive resin system was conducted according to four principal tasks: 1) synthesis of candidate resins, 2) curing studies, 3) screening studies and 4) detailed characterization studies.

During the first task, twelve candidate resins were prepared from three readily available, multifunctional amino-alcohols and the acid chloride derivatives of four simple, unsaturated carboxylic acids. After screening several conventional amide-ester synthetic methods, a procedure involving the interfacial reaction of an aqueous solution of an amine-alcohol, with a tetrahydrofuran solution of an acid chloride, was chosen as the standard preparative method. This method was found to offer the best balance of high yield, short reaction time and ease of product recovery.

The candidate resins were characterized for correct structure by infrared and nuclear magnetic resonance spectroscopy. They were found to be >95% pure and free of unreacted starting materials by thin layer chromatographic analysis. In all instances, the resins were moderately viscous liquids at room temperature.

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of curing agents representing a variety of chemical types and activities. By contrast, the A and B derived resins could be cured in less than 24 hours with conventional peroxide/activator cure systems such as methyl ethyl ketone peroxide/cobalt naphthanate (MEKP/CN) or N,N-dimethylaniline/benzoyl peroxide (DMA/BP).

The screening studies employed aluminum/titanium bimetallic curvature measurement specimens to aid in a preliminary evaluation of the candidate resins in terms of cure completion, adherence and resin/metal interactions. The test was performed by heating the specimens bonded with the resins for 16 hrs. at 344 K (160°F), in an oven, allowing them to cool and examining them for residual curvature adhesion and mode of bond rupture when separated.

The bimetallic strips bonded with the six candidate A and B resins were free of residual curvature, indicating that no further cure occurred in the hot air oven. Separation of the strips resulted in bond failure that was principally (>70%) cohesive in nature. Where evidence of adhesive failure was noted it was found at the aluminum surface. There was no evidence of deleterious adhesive/metal interactions.

The final portion of the program, the detailed characterization studies, were designed to assess the adhesion, thermo-oxidative stability and moisture sensitivity of the candidate resins. The results of these studies were used to rank the resins and aid in the selection of the three most promising candidates.

To test the moisture sensitivity of the resins, they were used to bond pairs of aluminum strips, which were then immersed in boiling water for two hours. The test specimens were monitored for retention of adhesive bond integrity and for changes in weight. The results of these tests served to differentiate clearly between the moisture sensitivity of the acrylic and methacrylic resins in that all of the former remained intact and suffered weight losses of less than 0.1%, whereas all of the specimens bonded with the B resins separated during the immersion or suffered severe loss of bond strength.

The acrylic acid derived resins also showed their superiority in lap-shear strength tests. All of the A resins had room temperature lap-shear strengths with aluminum adherends in excess of  $7.6 \times 10^6 \text{ N/m}^2$  (1100 psi),



whereas the B resin bonded coupons failed at  $5.3 \times 10^6 \text{ N/m}^2$  (770 psi) or less. The generally superior performance of the A resins is probably due to greater adhesion to the aluminum substrates.

The results of the detailed characterization studies clearly identify the three resins employing acrylic acid acyl components as the most promising candidate resins for further development as fully formulated adhesives.

The body of this final report is divided into four sections covering the program technical tasks: (Section II) TASK I - Synthesis of Candidate Resins, (Section III) TASK II - Curing Studies, (Section IV) TASK III - Screening Studies and (Section V) TASK IV - Detailed Characterization Studies. Section VI is devoted to a presentation of the principal conclusions reached as a result of this feasibility study along with recommendation for further study. The information provided in the body of this report is supplemented by detailed accounts of experimental procedures in the Appendix.

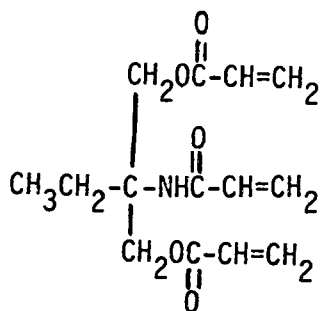
## II. TASK I - SYNTHESIS OF CANDIDATE RESINS

The objective of this task was the preparation of samples of the candidate resins to be assessed during this feasibility study. Seven commercially available resin precursors were selected as building blocks that could be joined in a variety of combinations to impart a broad range of physical and chemical properties to the resins and cured adhesives. For the purposes of this feasibility study, the resin syntheses were performed with acid chloride derivatives of the carboxylic acids to take advantage of the simple and rapid acylation afforded by those reactive species.

Details of the Task I resin synthesis studies are presented below. Representative synthetic procedures and supporting analytical data may be found in the Appendix.

### 2.1 RESIN PRECURSORS

The seven resin precursors which were combined to prepare the twelve resins proposed for study during this program are shown in Table I. Each of the four acyl and three amine-alcohol components was assigned a letter designation in the table (e.g., A = acrylic, E = 3-amino-1,2-propanediol, etc.) which, for the sake of brevity, will be employed in the remainder of this report for identification of all resin components. For example, resin A-G refers to the acrylic diester-amide of 2-amino-2-ethyl-1,3-propanediol, shown in the structure below:



Resin A-G

TABLE I  
Resin Starting Ingredients

Ingredient Type	Name	Structure	Alphabetical Designation
<u>Acids</u>	Acrylic acid	$\text{CH}_2=\text{CHCO}_2\text{H}$	A
	2-Methyl acrylic acid (methacrylic acid)	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_2=\text{CCO}_2\text{H} \end{array}$	B
	3-Methyl acrylic acid (crotonic acid)	$\text{CH}_3\text{CH}=\text{CHCO}_2\text{H}$	C
	Vinylacetic acid (3-butenic acid)	$\text{CH}_2=\text{CHCH}_2\text{CO}_2\text{H}$	D
<u>Amine-Alcohols</u>	3-Amino-1,2-propanediol	$\begin{array}{c} \text{HOCH}_2\text{CHCH}_2\text{NH}_2 \\   \\ \text{OH} \end{array}$	E
	Tris-(hydroxymethyl)aminomethane	$(\text{HOCH}_2)_3\text{CNH}_2$	F
	2-Amino-2-ethyl-1,3-propanediol	$\begin{array}{c} \text{NH}_2 \\   \\ \text{HOCH}_2-\text{C}-\text{CH}_2\text{OH} \\   \\ \text{C}_2\text{H}_5 \end{array}$	G

All of the resin starting materials were purchased from commercial sources. The amino-alcohols were assayed by thin layer chromatography (tlc) and neutralization equivalent titration and all were found to exceed the minimum 90% purity specification for use in resin synthesis. The acyl components were purchased as the acid chloride derivatives and were also found to be of greater than 90% purity by chloride analysis. Since the precursors met or exceeded the minimum purity standards as received, no further purification was undertaken.

## 2.2 RESIN SYNTHESIS

The effort to prepare the candidate resins was begun by screening several conventional amide-ester synthetic methods to find one that would serve, with appropriate minor modifications, as a standard preparative procedure for the resins to be used in the cure studies (Task II). Resin A-G was employed as the model system for the two solution and two interfacial methods investigated. The results of the experiments are shown in Table II. The solution reactions were performed in round bottomed flasks under nitrogen with mechanical agitation. The interfacial reactions were performed in blenders by rapidly adding a solution of the acid chloride in the organic solvent to an aqueous solution of the amine-alcohol containing an inorganic acid acceptor. The procedures used for these test reactions were modeled after examples found in Reference 1.

The tetrahydrofuran (THF)/H<sub>2</sub>O interfacial method was chosen as the standard preparative method for the preparation of the candidate resins used in the study because of the relatively good yields, short reaction time and ease of product recovery. Although the resin yield in the solution reaction employing dimethylacetamide (DMAC) was higher, the relatively high boiling point of the solvent (439 K/330°F) greatly increases the danger of polymerizing the resins during isolation. A detailed experimental procedure representative of those employed for the preparation of all of the candidate resins is presented in the Appendix.

Table III shows the yields typically obtained for the resins using the standard procedure. Since the primary concern of the Task I synthesis work was to prepare small (ca. 0.5 mole) resin samples for the Task II cure

TABLE II  
SCREENING OF RESIN PREPARATIVE METHODS

Resin <sup>a</sup>	Method	Solvent <sup>b</sup>	Acid Acceptor	Reaction Temp. (°K)	Reaction Time (Hrs)	Yield
A-G	Interfacial	CH <sub>2</sub> Cl <sub>2</sub> /H <sub>2</sub> O	Na <sub>2</sub> CO <sub>3</sub>	293	0.5	5.7 <sup>c</sup>
A-G	Interfacial	CH <sub>2</sub> Cl <sub>2</sub> /H <sub>2</sub> O	Na <sub>2</sub> CO <sub>3</sub>	293	0.5	6.4 <sup>c</sup>
A-G	Solution	Ethyl Ether	Triethylamine	293/ 308	4.0/ 0.5	12.0
A-G	Interfacial	THF/H <sub>2</sub> O	NaOH	293	0.5	46.0
A-G	Interfacial	THF/H <sub>2</sub> O	NaOH	293	0.25	41.0
A-G	Solution	DMAC	DMAC	293	1.0	48.0

<sup>a</sup>See Table I for resin code

<sup>b</sup>THF = tetrahydrofuran; DMAC = dimethylacetamide

<sup>c</sup>Replicate reactions

TABLE III  
RESIN YIELDS FROM STANDARD PROCEDURE

RESIN <sup>a</sup>	YIELD (%)
A-E	50
A-F	54
A-G	52
B-E	95
B-F	67
B-G	99
C-E	41
C-F	64
C-G	59
D-E	44
D-F	74
D-G	61

<sup>a</sup>See Table I for resin code.

<sup>b</sup>See Appendix for standard preparation procedure.

studies, a concerted effort to maximize resin yield was not made during this program. It is believed that an effort of that sort would be more profitably undertaken after the feasibility of this new family of adhesives is demonstrated and the most promising resins are selected. At that point larger quantities of material will be needed for in depth study and optimization and a more economical route will be required.

The candidate resins are clear, yellow to light brown, viscous liquids at room temperature. The resins containing A (acrylic) and B (methacrylic) acyl components which have vinyl unsaturation are, as might be expected, more susceptible to premature polymerization than the C and D resins containing allylic functions. Gellation occurred in several instances during product isolation or storage in a refrigerator at 273 K (32°F). It was found that inclusion of 0.3% by weight (based on theoretical yield) of an autioxidant (2,6-di-tert-butyl-4-methyl-phenol,"Ionol") before final isolation of the A and B resins provided sufficient protection to assure a storage life of greater than one month at 273 K. Addition of an antioxidant to the less reactive C and D resins was found to be unnecessary.

The molecular structures of the resins were confirmed by their infrared spectra (ir) which showed the characteristic absorption bands for amide, ester and double bond functionality, and by their nuclear magnetic resonance spectra (nmr). The ir and nmr spectra of the twelve candidate resins may be found in the Appendix. Thin layer chromatograms (tlc) of the resins indicated that they were all >95% pure, and free of unreacted starting materials. The minor components present in the resins displayed essentially the same elution behavior (i.e., similar  $R_f$ ) as the major components and probably represent partially acylated amine-alcohols.

### III. TASK II - CURING STUDIES

The Task II curing studies were directed toward defining the most satisfactory resin curing agents and cure conditions for each resin system to facilitate a preliminary ranking of the candidates in Task III (Section IV).

The discussion of the curing studies, presented below, is organized in two subsections. The first describes the main study in which two conventional peroxide/activator systems, methyl ethyl ketone peroxide/cobalt naphthanate (MEKP/CN) and N,N-dimethylaniline/benzoyl peroxide (DMA/BP), were tested. The second subsection describes supplementary studies employing a variety of catalyst types in an effort to effect room temperature cure with the relatively unreactive C and D resins.

#### 3.1 MAIN CURING STUDIES

The curing reactions were conducted for 6, 24 and 48 hours on each resin in the presence of 1%, 3% and 5% (w/w) of each activator catalyst system (a total of 9 samples for each resin-catalyst set). The tests were performed by mixing the appropriate quantities of an activator-catalyst system with a weighed sample of a resin, dividing the mixture into three approximately equal portions and then placing the portions on a glass grid. If an experimental sample showed evidence of cure (solidification with little or no tack) after the designated reaction time, it was placed in a sufficient quantity of concentrated (36 N) sulfuric acid to produce a 0.5% (w/w) solution if it dissolved. A sample was considered to be cured if it retained its integrity after two hours at room temperature (293 K/68°F) in the sulfuric acid. If more than 50% of the sample remained undissolved after two hours in the acid it was considered to be partially cured. Dissolution of more than 50% of a sample was designated as evidence of no cure. The results of the curing experiments performed with methyl ethyl ketone peroxide/cobalt naphthanate (MEKP/CN) and N,N-dimethylaniline/benzoyl peroxide (DMA/BP) are shown in Table IV.

The tested candidate resins which possess vinyl cure sites, i.e., A and B resins, cured more rapidly than the allylic C and D resins. This behavior is in keeping with the known relative reactivity of vinylic and



TABLE IV  
RESULTS OF CURING STUDIES<sup>a</sup>

Resin <sup>b</sup>	Minimum Time For Cure (Hrs)					
	MEKP/CN <sup>c</sup>			DMA/BP <sup>d</sup>		
	1%	3%	5%	1%	3%	5%
A-E	NC <sup>e</sup>	24	6	48 <sup>f</sup>	6 <sup>g</sup>	6 <sup>g</sup>
A-F	NC	NC	24	6	6 <sup>g</sup>	6 <sup>g</sup>
A-G	NC	48	6	48 <sup>f</sup>	6 <sup>g</sup>	6 <sup>g</sup>
B-E	NC	48 <sup>f</sup>	24	NC	6 <sup>g</sup>	6 <sup>g</sup>
B-F	NC	48 <sup>f</sup>	24	NC	6 <sup>g</sup>	6 <sup>g</sup>
B-G	NC	48 <sup>f</sup>	24	NC	6 <sup>g</sup>	6 <sup>g</sup>
C-E	NC	NC	NC	NC	NC	NC
C-F	NC	NC	NC	NC	NC	NC
C-G	NC	NC	NC	NC	NC	NC
D-E	NC	NC	NC	NC	NC	NC
D-F	NC	NC	NC	NC	NC	NC
D-G	NC	NC	NC	NC	NC	NC

<sup>a</sup>Cure studies performed at 293 K (68°F) in air. The A & B resins contained 0.3% by weight Ionol stabilizer.

<sup>b</sup>See Table I for resin code.

<sup>c</sup>Methyl ethyl ketone peroxide/cobalt naphthanate.

<sup>d</sup>N,N-Dimethylaniline/benzoyl peroxide.

<sup>e</sup>NC = no cure; more than 50% dissolved in concentrated sulfuric acid.

<sup>f</sup>Partial cure; less than 50% dissolved in concentrated sulfuric acid.

<sup>g</sup>Exothermic reaction on mixing.

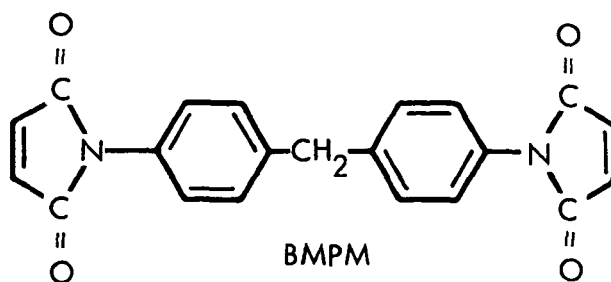
allylic double bonds towards free radical agents. With the exception of resin D-F, which gradually gelled over a period of five days, none of the C and D resins gave evidence of polymerization in the presence of the MEKP/CN and DMA/BP catalyst/activator systems.

On the basis of these studies, 5% by weight MEKP/CN was chosen as the catalyst formulation for use with the A and B resins in the Task III screening studies. Smaller concentrations of MEKP/CN cured too slowly when sufficient (0.3% w/w) Ionol stabilizer was present to provide adequate shelf life. The other cure system tested, N,N-dimethylaniline/benzoyl peroxide, proved to be excessively energetic, causing very rapid, exothermic gelation with most of the candidate resins.

### 3.2 SUPPLEMENTARY CURING STUDIES

Several other cure methods (not shown in Table IV) were assessed in an effort to effect room temperature cure of the C and D resins in 48 hours or less. The most successful system employed involved the use of bis(4-maleimidophenyl)methane(BMPM). The structure of this material is shown below. It functions as an unsaturated cocuring agent, in conjunction with methyl ethyl ketone peroxide/cobalt naphthanate (MEKP/CN). A C-F resin containing 5% by weight of BMPM-MEKP-CN cured gradually over a four day period. Other cure systems that were screened included: divinyl cocuratives (divinylbenzene-MEKP/CN), hydroperoxide/activators (*tert*-butyl hydroperoxide/CN and *tert*-butyl hydroperoxide/formamide), Lewis acid ( $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ ), strong acid (trifluoroacetic acid), strong base (calcium hydride and sodium methoxide) and redox (ferrous ammonium sulfate/ascorbic acid). All of the agents were tested at the 5% by weight level, both in air and anaerobically.

In view of the difficulties encountered in effecting acceptable room temperature cures with the C and D resins, and with the concurrence of the NASA Technical Monitor, curing studies on these resins were de-emphasized in favor of greater concentration on the remaining program tasks.



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#### IV. TASK III - SCREENING STUDIES

The screening studies task employed titanium/aluminum bimetallic curvature measurement specimens to aid in a preliminary evaluation of the candidate resins in terms of cure completion, adherence and resin/metal interactions. This relatively rapid and simple test was designed to uncover gross deficiencies in any of the candidates before subjecting them to more extensive testing in Task IV.

The test specimens were prepared by spreading a candidate resin/catalyst composition on the surface of matching, specially cleaned (the cleaning procedure is described in the Appendix), 0.15-m x 0.013-m x 0.0013-m (6.0-in x 0.5-in x 0.05-in) strips of 6Al-4V titanium and 2024 T-4 aluminum. The coated surfaces were placed together and the resin was allowed to cure for 24 hours at room temperature under  $1.1 \times 10^4 \text{ N/m}^2$  (1.6 psi) pressure. The bimetallic strip was then heated in an air oven at 344 K (160°F) for 16 hours. After the test specimen had cooled to ambient room temperature, it was examined for residual curvature, adhesion and mode of bond rupture when separated.

The bimetallic strips bonded with the six A and B candidate resins were free of residual curvature, indicating that no further cure occurred in the hot air oven. Separation of the strips resulted in bond failure that was principally (>70%) cohesive in nature. Where evidence of adhesive failure was noted it was found at the aluminum surface. There was no evidence of deleterious adhesive/metal interactions. A representative example (bonded with resin B-G) of the appearance of the bimetallic strips after the heating treatment is shown in Figures 1 and 2. Since all of the A and B resins showed acceptable behavior in these tests, they were all subjected to the detailed characterization studies described in Section V.

Although the C and D resins failed to cure during the Task II curing studies, a bimetallic curvature measurement specimen was prepared with the C-D material and 5% by weight MEKP/CN to test the effect of higher temperature. Unfortunately, the C-F resin specimen remained uncured even after completion of the 16-hour heating period.

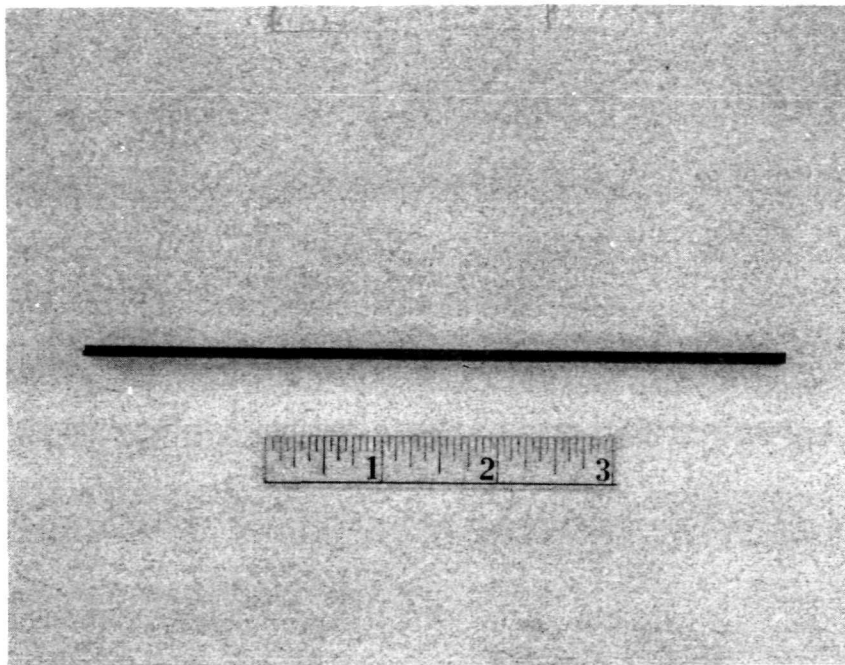


Figure 1. Edge View of Bimetallic Curvature  
Measurements Specimen (B-G Resin)  
After 344°K/16 hr Heat Treatment

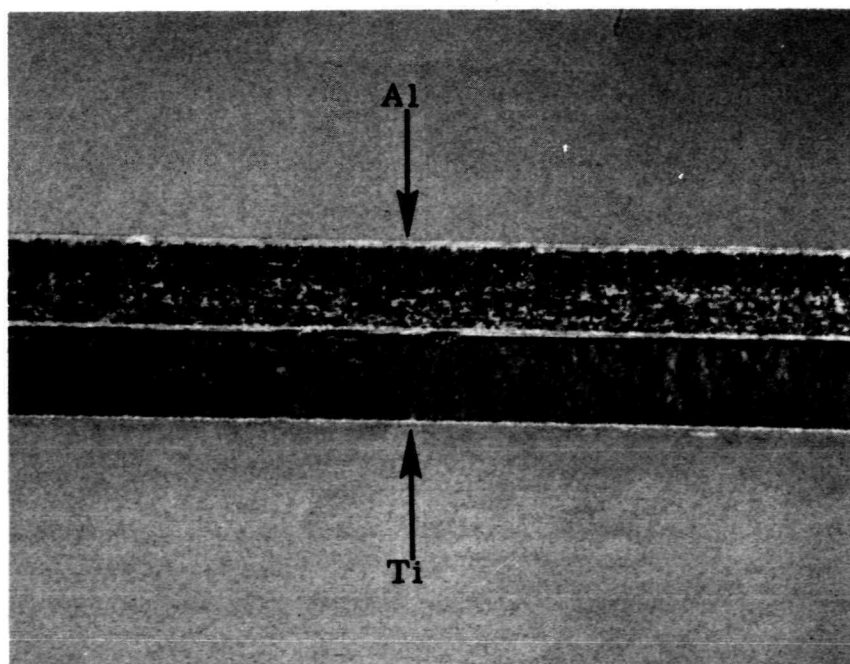


Figure 2. Detail (10 x magnification) of Edge of  
Bimetallic Curvature Measurement Specimen  
(B-G Resin) After 344 K/16 hr Heat Treatment

## V. TASK IV - DETAILED CHARACTERIZATION STUDIES

The Task IV detailed characterization studies were designed to assess the adhesion, thermo-oxidative stability, and moisture sensitivity of the candidate resins. The results of these studies were used in the final ranking of the resins and aided in the selection of the three most promising candidates.

The tests employed in this task included a water boil moisture sensitivity test, described in Section 5.1 and room temperature lap-shear strength measurements described in Section 5.2. The effect of moisture and heat aging on the lap-shear strengths of coupons bonded by the candidate resins are described in Sections 5.3 and 5.4, respectively. The results of the first two tests (water boil and room temperature lap-shear) clearly established the superiority of the A resins, and only those materials were subjected to the second two, more time consuming, tests.

### 5.1 MOISTURE SENSITIVITY TESTS

In order to assess the moisture sensitivity of the resins qualitatively, they were used to bond pairs of aluminum strips, which were monitored for retention of adhesive bond integrity and for changes in weight after immersion in boiling water for two hours. To prepare the test specimens, the aluminum strips were cleaned and then bonded with the candidate resins using the techniques described in the Appendix for the preparation of curvature measurement specimens. After cure was complete, the bonded test strips were dried in a circulating-air oven for two hours at 373 K (212°F). The dried strips were weighed, immersed in boiling water for two hours, dried and then weighed again.

The results of the moisture sensitivity tests of the A and B resins are shown in Table V. The adhesive bonds of all of the A resins and BF remained intact and suffered resin weight losses of less than 0.1%. The BE and BG specimens separated before the end of the two hour water boil. The bond strength of the BG specimen that survived the test was significantly reduced by the exposure, but there was no apparent swelling of the resin and very little weight loss.

Table V  
Moisture Sensitivity Tests

Resin System <sup>d</sup>	Weight Loss (%) <sup>a</sup>
AE	0.0640
AF	0.0156
AG	0.0741
BE	b
BF	0.0278
BG	0.0156 <sup>c</sup>

- a. After 2-hour immersion in boiling water; duplicate runs.
- b. Both specimens separated after 90 min.
- c. One specimen separated after 105 min.
- d. See Table I for resin code.

## 5.2 ROOM TEMPERATURE LAP-SHEAR STRENGTH

To perform the lap-shear strength tests, aluminum lap-shear coupons were cleaned in the same manner as the curvature measurement strips (see Appendix for procedure) and then primed with a thin coat of the test resin. A 0.025-m x 0.051-m (1-in x 2-in) piece of 120 style glass cloth was immediately placed on the primed surface and then impregnated with the resin. The lap-shear coupon was then assembled with a bonded overlap area of 0.013-m x 0.025-m (1/2-in x 1-in) and cured under a pressure of  $3.4 \times 10^4$  N/m<sup>2</sup> (5 psi) for 24 hr. The specimens were tested according to Federal Test Method Standard No. 175.

The results of the lap-shear strength tests of the A and B resins, cured with 5% by weight MEKP/CN are shown in Table VI. All of the A resins displayed lap-shear strengths in excess of  $7.6 \times 10^6$  N/m<sup>2</sup> (1100 psi), whereas the B resin bonded coupons had strengths of  $5.3 \times 10^6$  N/m<sup>2</sup> (770 psi) or less. The generally superior performance of the A resins is probably due to greater adhesion to the aluminum substrates. That interpretation is supported by evidence for 90-100% adhesive failure for the B resins, whereas the principal failure mode for the A resin bonded coupons was cohesive. Further support for the contention of relatively poor B Resins aluminum adherence is found in their high moisture sensitivity,

reported in Section 5.1.

Lap-shear strength tests utilizing neat resins provide a useful guide to the property level that might be attained by a new material as a fully formulated adhesive, when they are compared with the results of neat resin tests of more mature products. In that context, the results of the lap-shear strength tests shown in Table VI are extremely encouraging. By contrast to strengths as high as  $11.7 \times 10^6 \text{ N/m}^2$  (1700 psi) for these new resins, lap-shear strengths of neat, room temperature cured epoxy resins are generally less than  $6.9 \times 10^6 \text{ N/m}^2$  (1000 psi) (Reference 2).

TABLE VI  
Lap-Shear Strength Tests<sup>a</sup>

Resin System <sup>b</sup>	Strength, <sup>c</sup> $\text{N/m}^2 \times 10^{-6}$ (psi)	
AE	8.7	(1260)
AF	11.7	(1700)
AG	7.6	(1100)
BE	5.3	( 770)
BF	4.4	( 640)
BG	3.1	( 455)

<sup>a</sup>Resins cured with 5% by weight MEKP/CN

<sup>b</sup>See Table I for resin code

<sup>c</sup>Triplicate breaks.

### 5.3 LAP-SHEAR STRENGTHS AFTER WATER BOIL

This portion of the detailed characterization studies was devoted to an assessment of the effect of moisture on the lap-shear strength of the most promising candidates. The high moisture sensitivity displayed by the B resins (see Section 5.1) precludes their testing by this method and only the A resins were included in the tests.

Aluminum lap-shear coupons, prepared as described in Section 5.2, were



immersed in boiling water for two hours. The specimens were then immersed in fresh distilled water at room temperature. After conditioning for at least 15 minutes the specimens were sponged dry and tested immediately at a loading rate of  $8.3 \times 10^6 \text{ N/m}^2$  (1200 psi) per minute. The results of these tests are shown in Table VII.

The A-G and A-F samples retained greater than 88% of their preimmersion strengths, confirming the low moisture sensitivity evidenced in the qualitative tests described in Section 5.1. The reason for the lesser strength retention (67%) of the A-E specimens is not clear. However, it should be noted that the strength of the control specimens was lower than those previously attained (compare with value in Table VI) and the proportion of adhesive failure was greater. Minor variations in properties such as these are typical of new materials for which optimized application procedures have not been developed.

#### 5.4 Lap-Shear Strengths After Heat Aging

The effect of heat aging on lap-shear strength is shown in Table VII. For these tests, aluminum lap-shear coupons were heated for 300 hours at 340 K (160°F) in a circulating air oven. The lap-shear strengths of the specimens were determined at room temperature in the manner described above.

The A-F bonded specimens retained a creditable 78% of their original strength. The surprising result of apparent higher strength after heat aging for the A-G coupons is undoubtedly due to the property variations induced by non-optimized processing conditions mentioned in Section 5.3. The same phenomenon may be responsible for a portion of the 45% strength loss exhibited by the A-E specimens.

TABLE VII  
EFFECT OF WATER BOIL AND HEAT AGING  
ON LAP-SHEAR STRENGTHS

RESIN	LAP-SHEAR STRENGTH <sup>b</sup> N/m <sup>2</sup> x 10 <sup>-6</sup> (psi)		
	CONTROL	AFTER WATER BOIL <sup>c</sup>	AFTER HEAT AGING <sup>d</sup>
AE	7.0 (1020)	4.7 (690)	3.9 (560)
AF	12.0 (1750)	10.7 (1550)	9.5 (1370)
AG	4.6 (670)	4.1 (590)	5.8 (840)

<sup>a</sup>See Table I for resin code.

<sup>b</sup>Resin cured with 5% by weight MEKP/CN.

<sup>c</sup>Two hour immersion in boiling water.

<sup>d</sup>Aged for 300 hours at 344 K (160°F) in air.

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## VI. CONCLUSIONS AND RECOMMENDATIONS

Summarized below are the conclusions reached during this experimental study to determine the feasibility of a new approach for the development of stable, easily handled adhesive resins which will cure at ambient temperatures. Recommendations are made, based on the findings of this study, for further work to develop and optimize these new materials.

### 6.1 CONCLUSIONS.

1. Twelve members of this new family of adhesive resins were successfully prepared and their correct chemical structure was confirmed. All of the resins were liquids at room temperature, permitting their application without solvents.
2. Six of the resins, containing vinyl unsaturation were easily and completely cured at ambient room temperature in <48 hours using conventional free radical catalyst/activator systems.
3. The new resin systems show promise by virtue of:
  - Good adherence to Al and Ti.
  - Freedom from deleterious resin/metal interactions
  - Excellent resistance to water boil
  - Good lap-shear performance
4. The three most promising resin candidates are those obtained by the reaction of acrylic acid with the three amino-alcohols (i.e., the A resins) included in this study, by virtue of their superior moisture resistance and lap-shear strength test results.

### 6.2 RECOMMENDATIONS

1. Studies should be undertaken, using the three most promising resins identified during this program, to effect improvements in the following areas:
  - Optimization of resin mechanical properties for 219 K (-65°F) to 344 K (160°F) use

- Optimization of catalyst/accelerator/stabilizer combinations
  - Definition of minimum cure conditions in terms of time and temperature
  - Resin synthesis optimization in terms of yield, reproducibility and cost
  - Long term resin shelf stability
  - Long term isothermal aging and hydrolytic stability.
2. Adhesive development studies should be undertaken to test and evaluate the effects of standard formulary techniques on the properties of these resins. Such techniques would include:
- Metallic fillers (e.g., aluminum alloy powder)
  - Thixotropic agents (e.g., Cab-O-Sil)
  - Copolymers (e.g., amide resins)
  - Coupling agents (e.g., organic silanes)
  - Carriers (e.g., Style 104 glass scrim with various finishes).
3. The data obtained in the adhesive development study should be used to design and prepare an optimized adhesive formulation for detailed evaluation of:
- Residual stresses developed at elevated temperatures
  - Mechanical properties
  - Thermal and hydrolytic stability.

## APPENDIX

The standard preparative procedure used in the synthesis of the candidate resins used in this study is presented below, along with reproductions of the infrared and nuclear magnetic resonance spectra of the respective resins. The procedures used for preparing aluminum and titanium surfaces for the resins are also described.

### 1. STANDARD RESIN PREPARATIVE PROCEDURE

The following experimental procedure for the synthesis of resin A-G is representative of those employed for the preparation of all of the resins used in this study.

A cold (ca. 273 K) solution of 27.2 g (0.3 mole) of acryloyl chloride (A) in 60 ml of dry THF was poured all at once into a one-liter blender jar containing a vigorously agitated, cold (ca. 273 K) solution of 11.9 g (0.1 mole) of 2-amino-2-ethyl-1,3-propanediol (G) and 12.0 g (0.3 mole) of sodium hydroxide. During the reaction the blender jar was cooled with an ice-water jacket to maintain a reaction temperature  $\geq 293$  K (68°F). Mixing was continued for 10 minutes, then the solution was extracted twice with 300-ml portions of chloroform. The combined chloroform solutions were washed twice with saturated sodium bicarbonate solution and then dried over magnesium sulfate. Ionol antioxidant (0.08g) was added to the solution and then the chloroform was removed at room temperature under reduced pressure. The isolated resin was stored under nitrogen in a refrigerator at ca. 273 K (32°F).

The infrared (neat resin smears) and nuclear magnetic spectra of this and the other eleven candidate resins are presented in Figures 3-26, inclusive.

### 2. METAL SURFACE PREPARATION PROCEDURES

The following procedures were employed to clean the aluminum and titanium strip surfaces used in these studies.

Aluminum:

1. Vapor degrease - 1 min.
2. Chromic acid etch at 338 K - 343 K  
(149°F-158°F) - 12 min.
3. Cold tap water rinse - 3 min.
4. Distilled water soak - 6 min.
5. Repeat 3 and 4
6. Dry at 343 K (158°F) - 10 min.

Titanium:

1. Sandblast both sides
2. Soak in HTC Alkaline Clear at 343 K (158°F) -  
15 min
3. Hot tap water rinse - 3 min.
4. Cold tap water rinse - 3 min.
5. Coat with Pasa Jel - 20 min.
6. Cold tap water rinse - 3 min.
7. Distilled water rinse - 3 min.
8. Dry at 343 K (159°F) - 10 min.

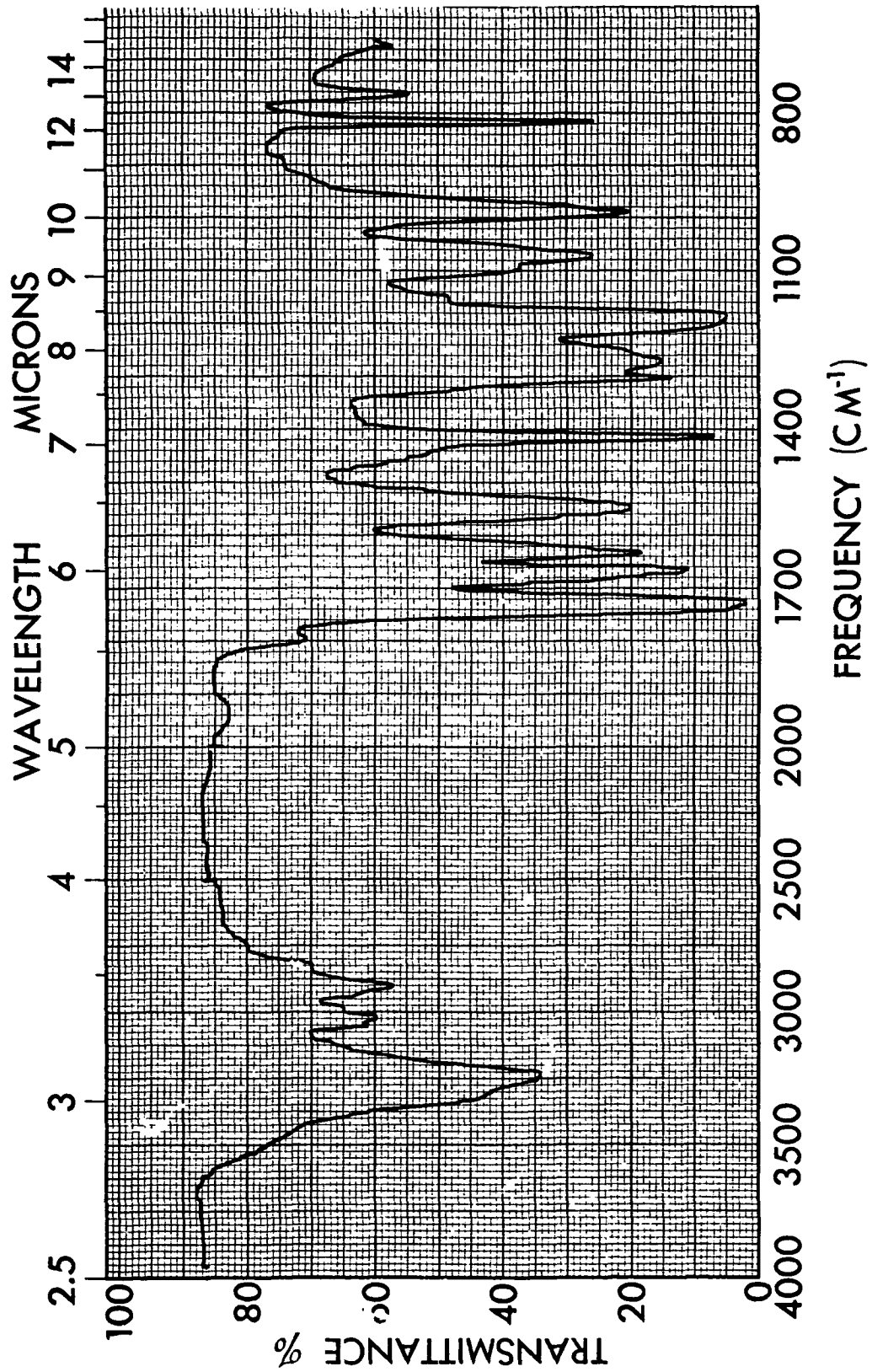


Figure 3. Infrared Spectrum of Resin A-E



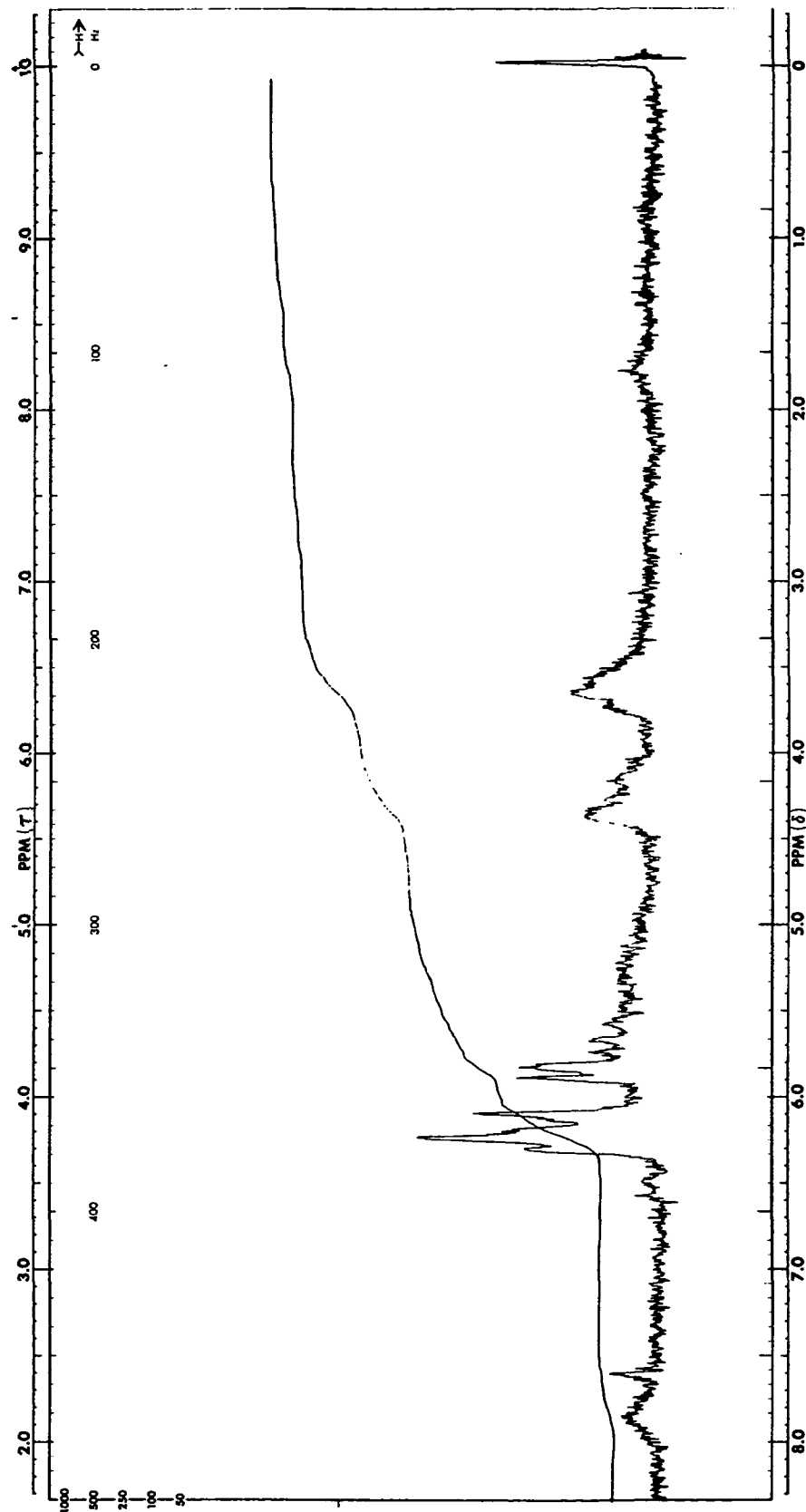


Figure 4. Nuclear Magnetic Resonance Spectrum  
of Resin A-E in CDCl<sub>3</sub>

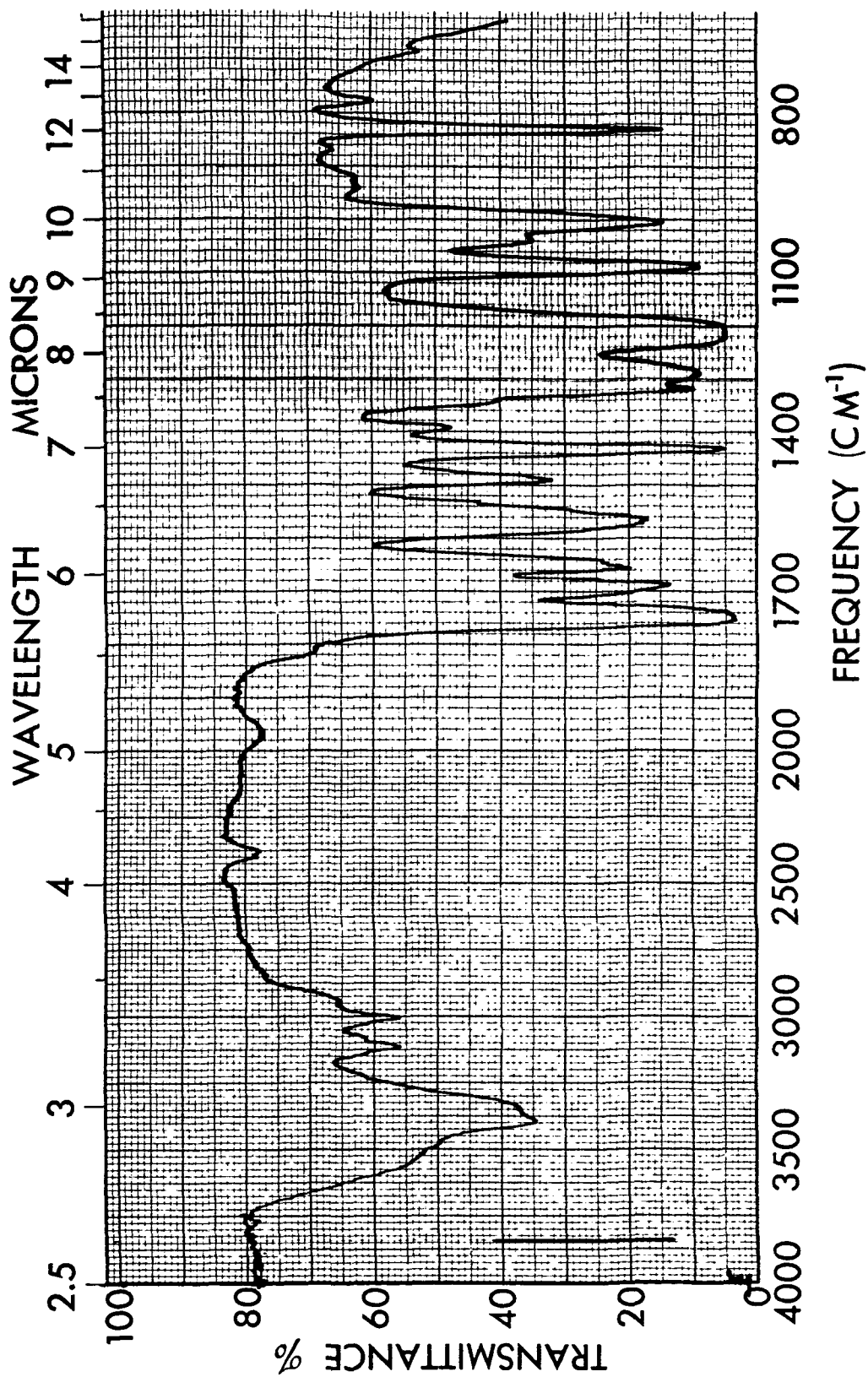


Figure 5. Infrared Spectrum of Resin AF

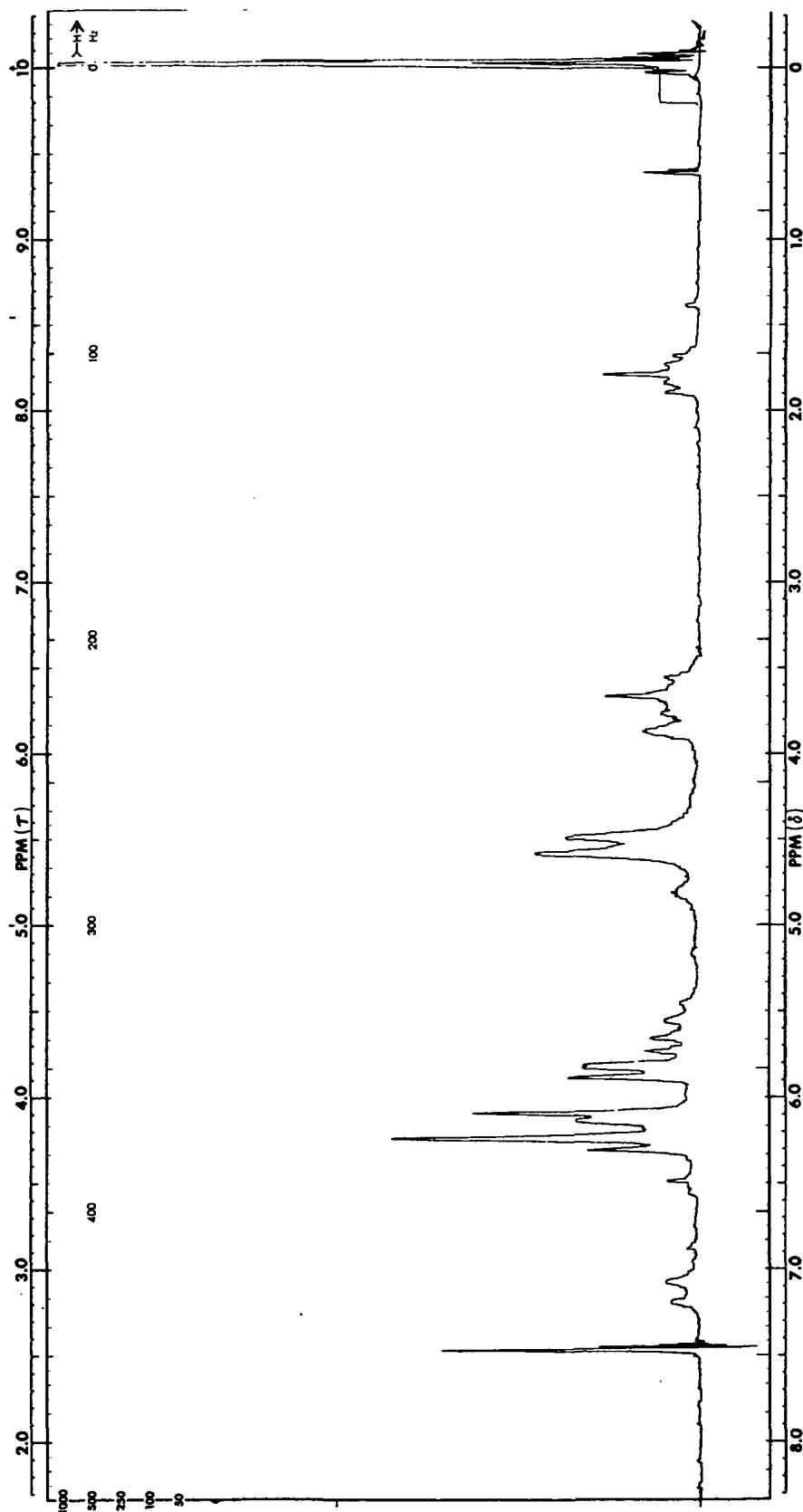


Figure 6. Nuclear Magnetic Resonance Spectrum  
of Resin A-F in  $\text{CDCl}_3$

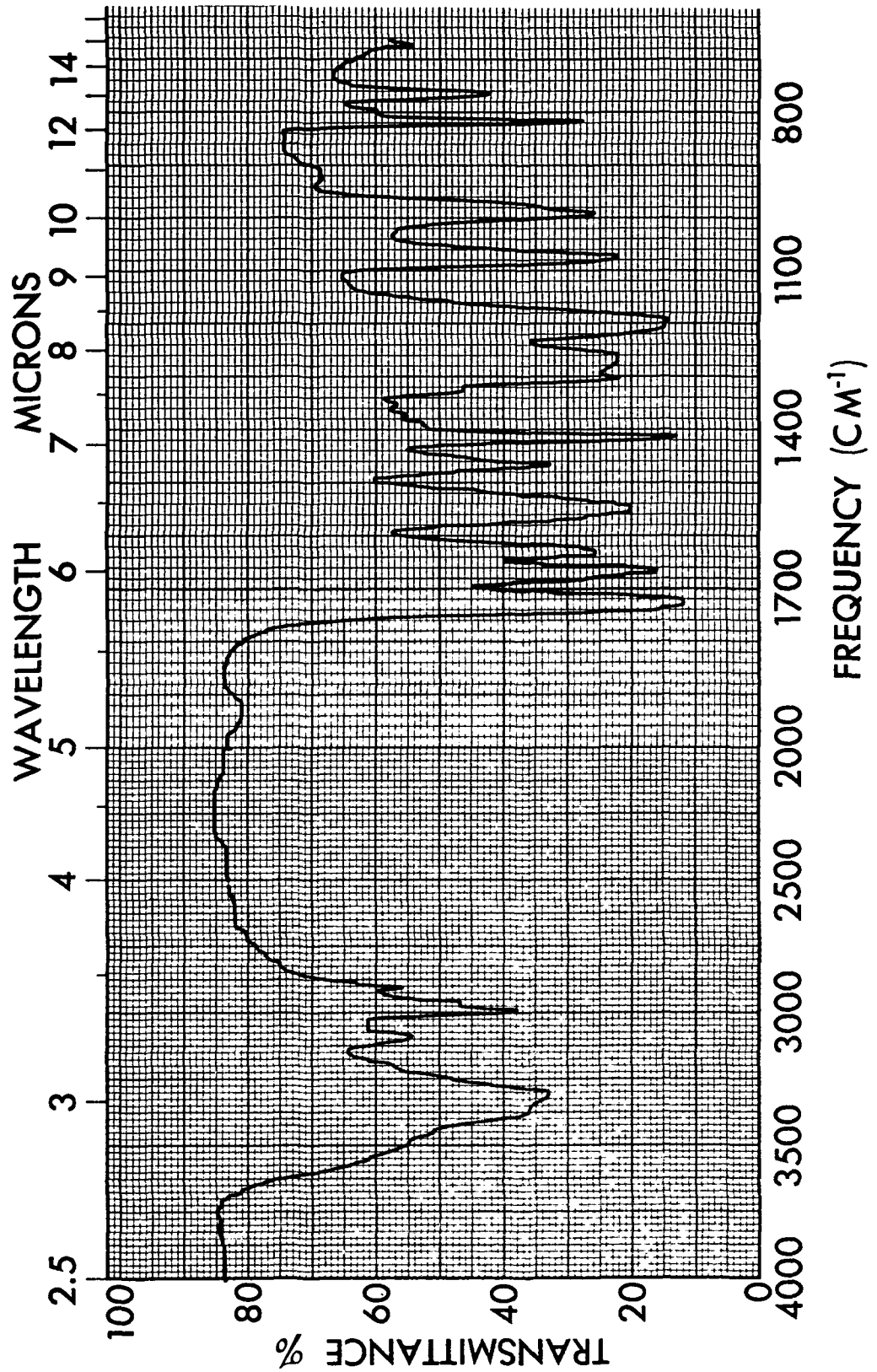


Figure 7. Infrared Spectrum of Resin AG

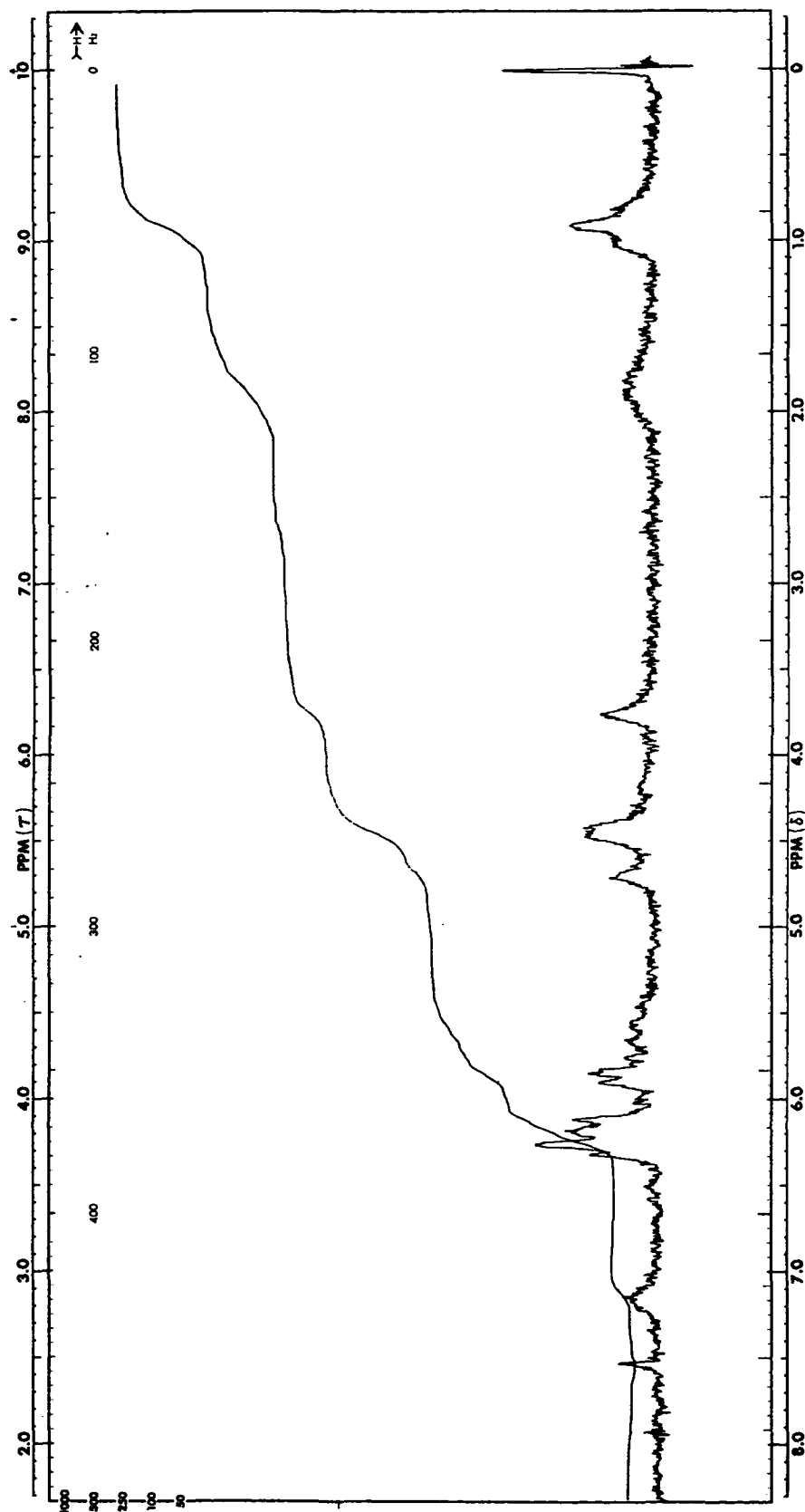


Figure 8. Nuclear Magnetic Resonance Spectrum  
of Resin A-G in  $\text{CDCl}_3$

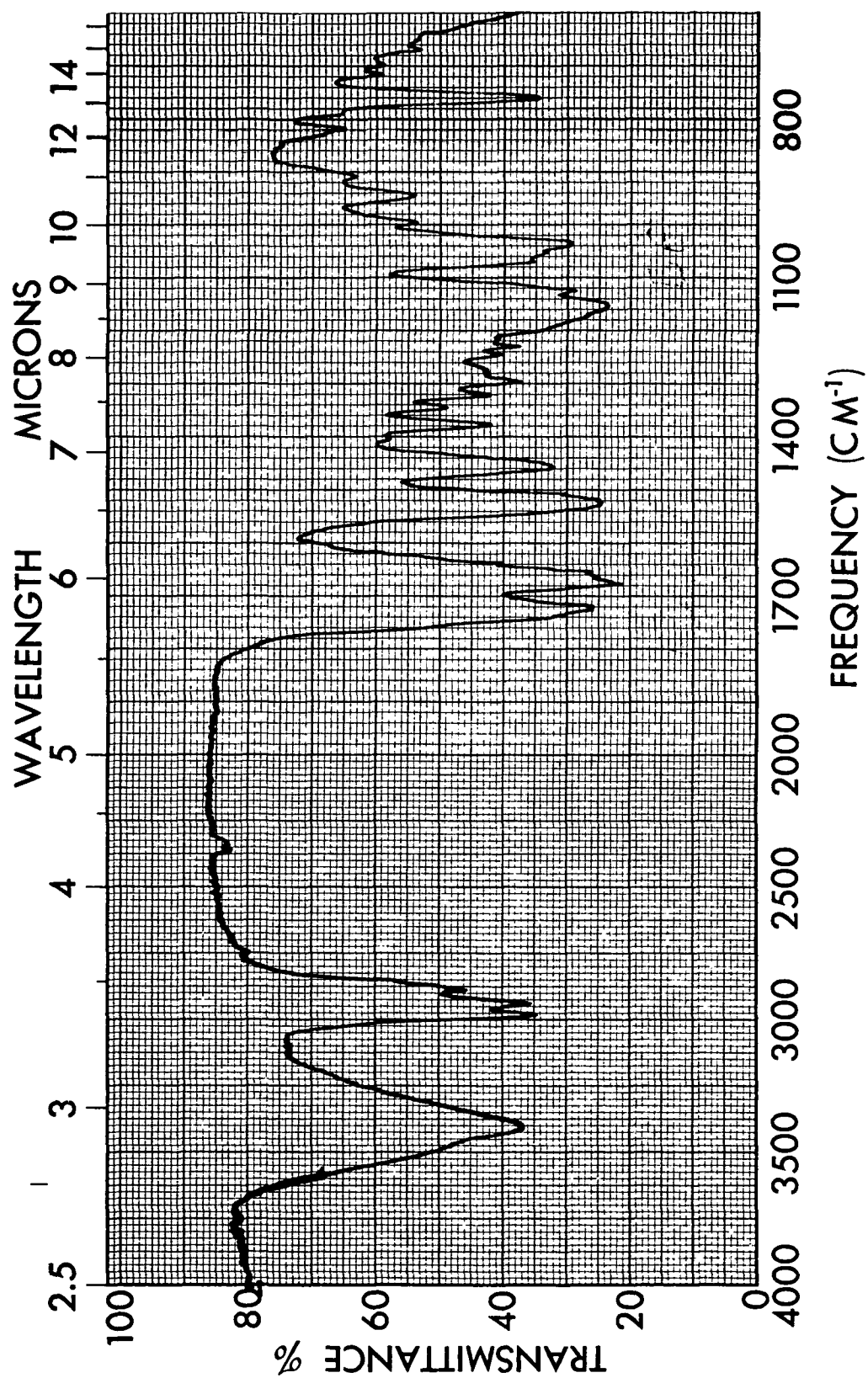


Figure 9. Infrared Spectrum of Resin B-E

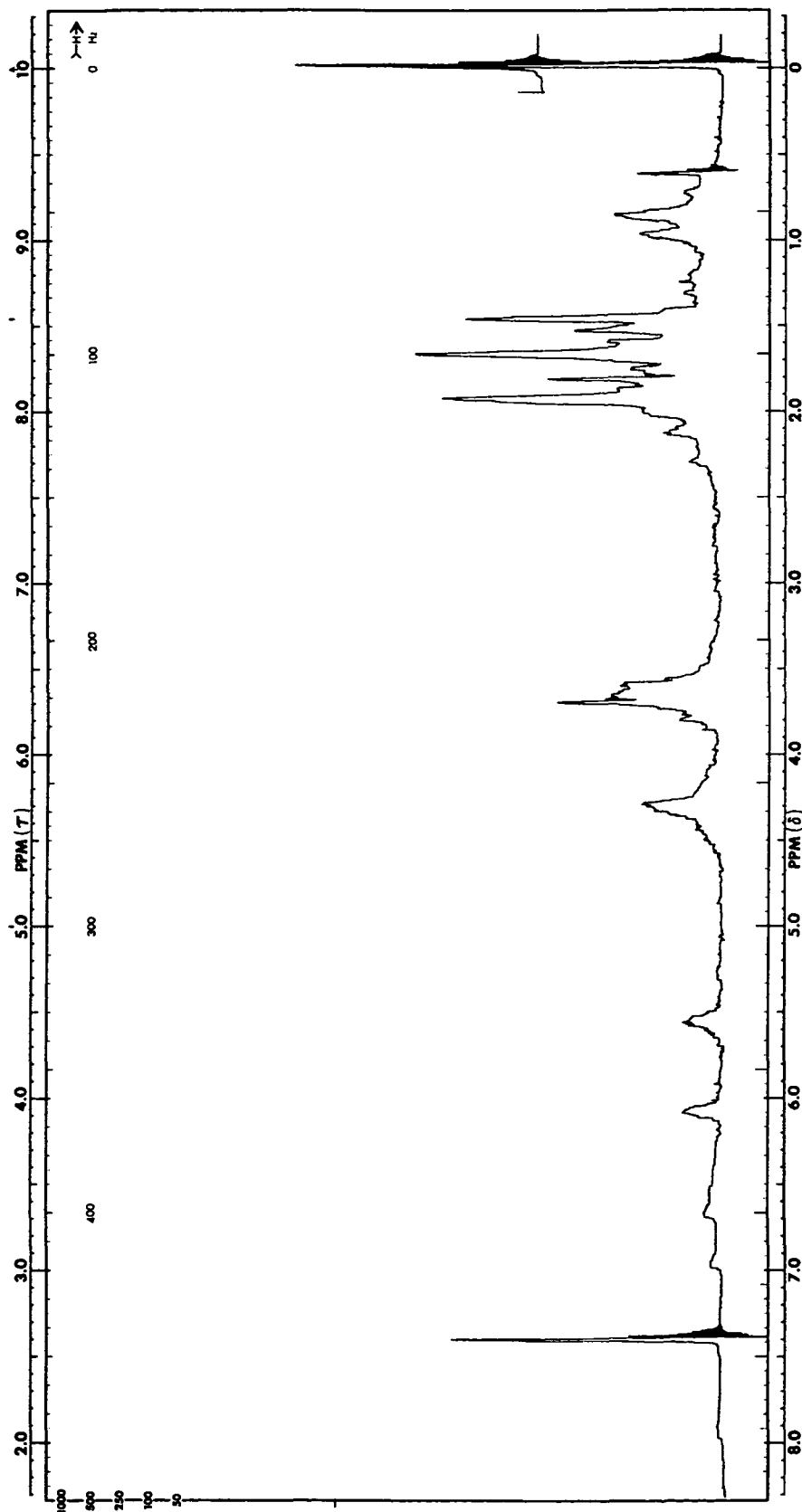


Figure 10. Nuclear Magnetic Resonance Spectrum  
of Resin B-E in  $\text{CDCl}_3$

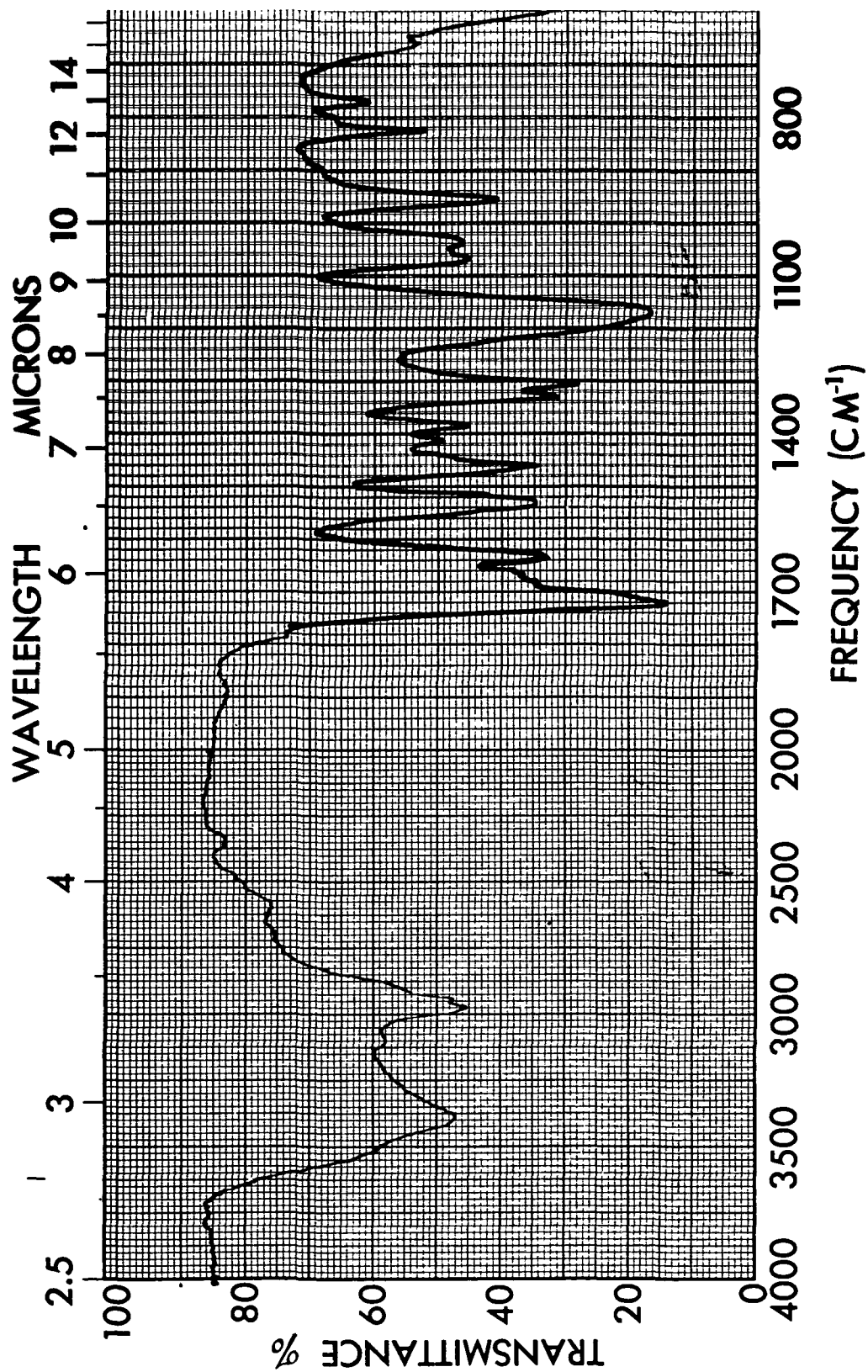


Figure 11. Infrared Spectrum of Resin B-F



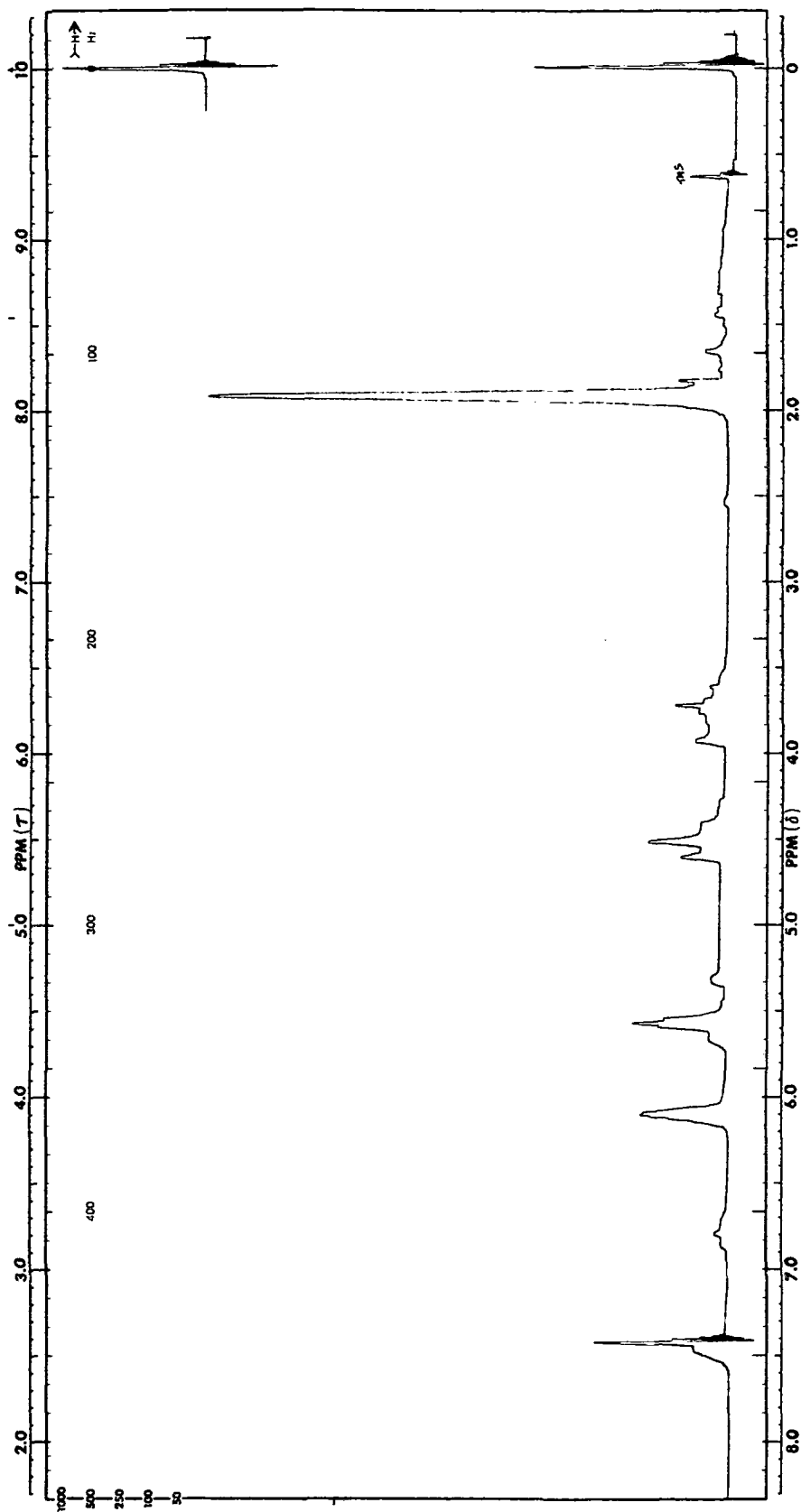


Figure 12. Nuclear Magnetic Resonance Spectrum  
of Resin B-F in CDCl<sub>3</sub>

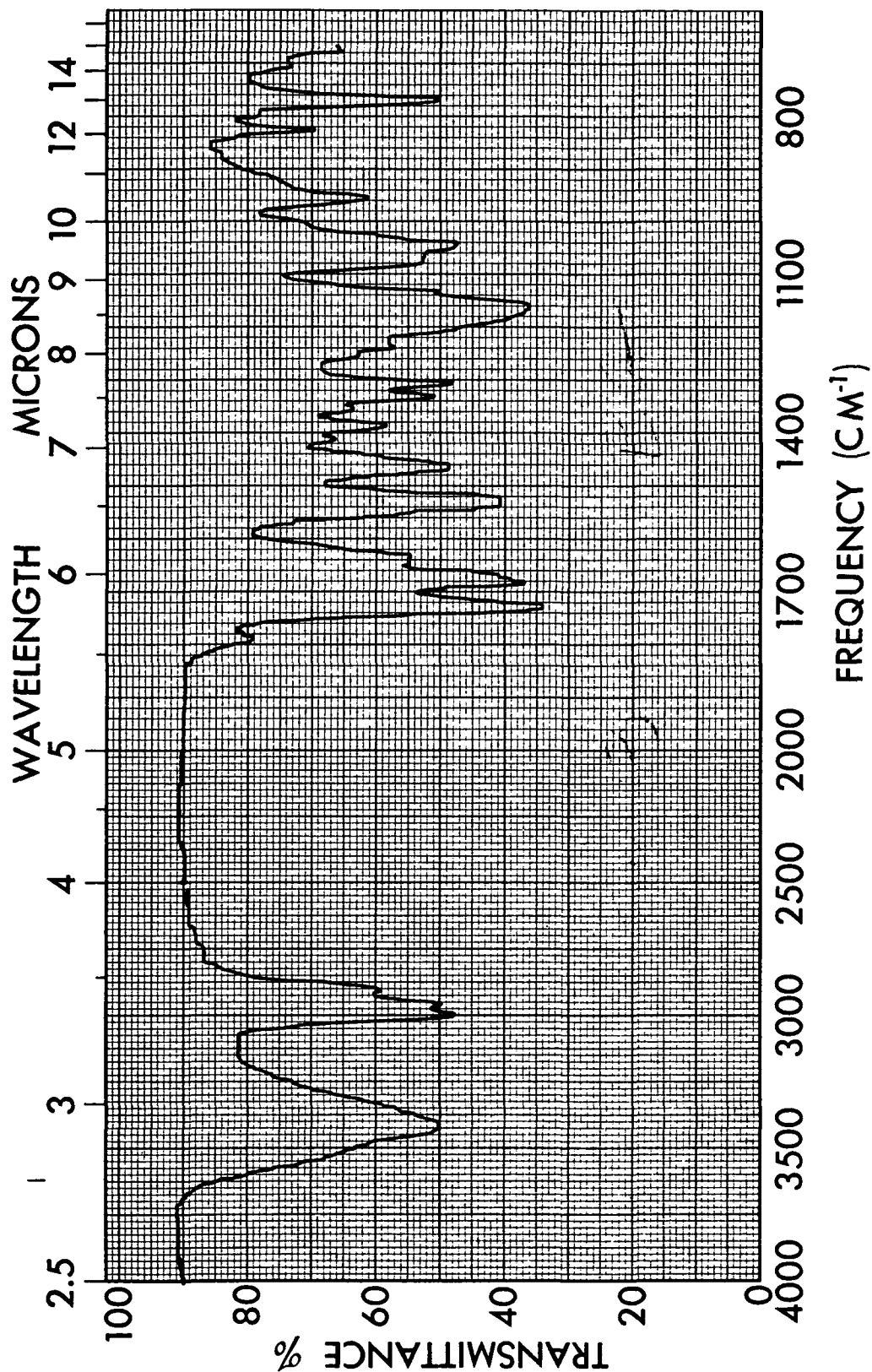


Figure 13. Infrared Spectrum of Resin B-G

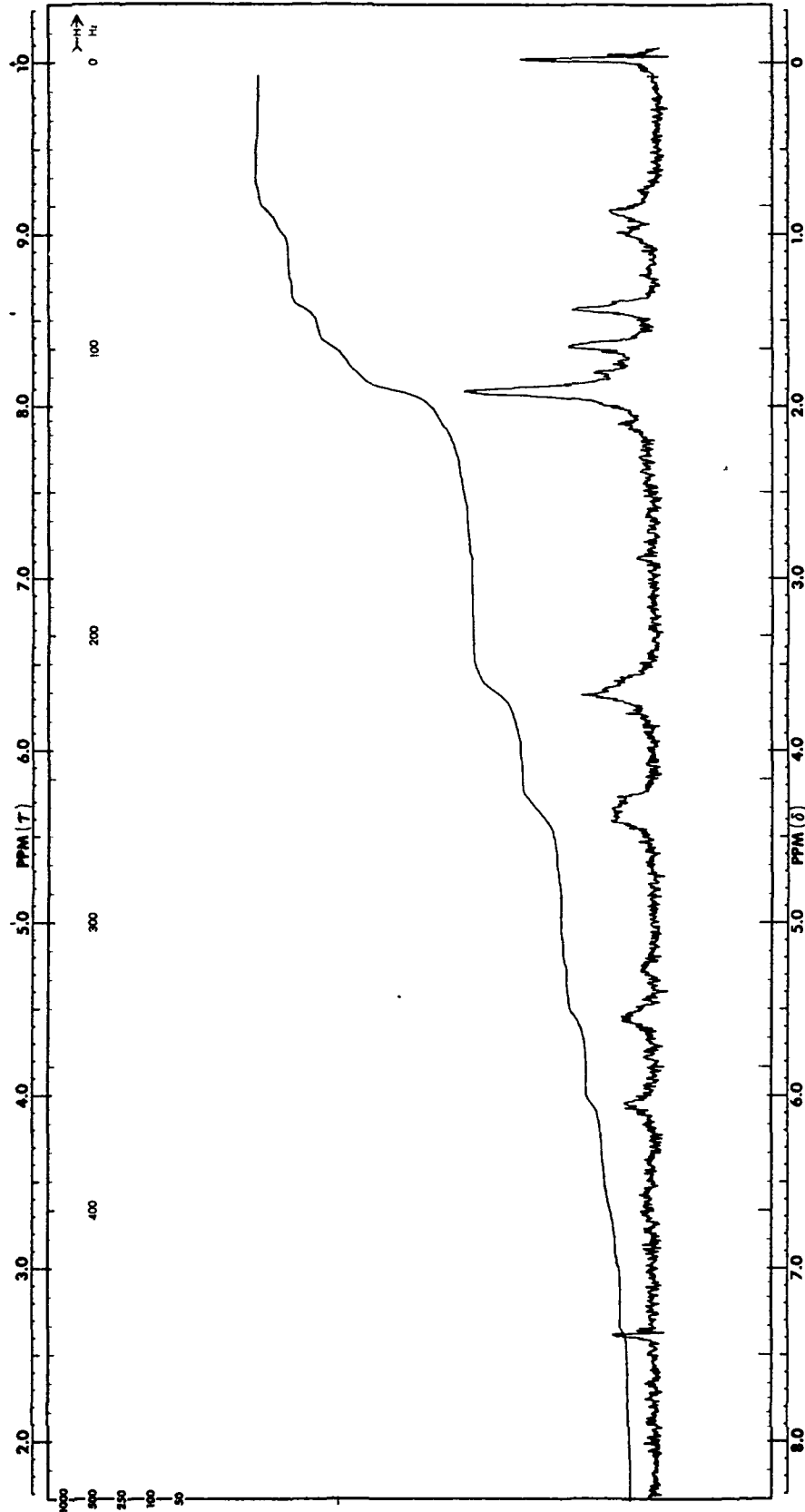


Figure 14. Nuclear Magnetic Resonance Spectrum  
of Resin B-G in CDCl<sub>3</sub>

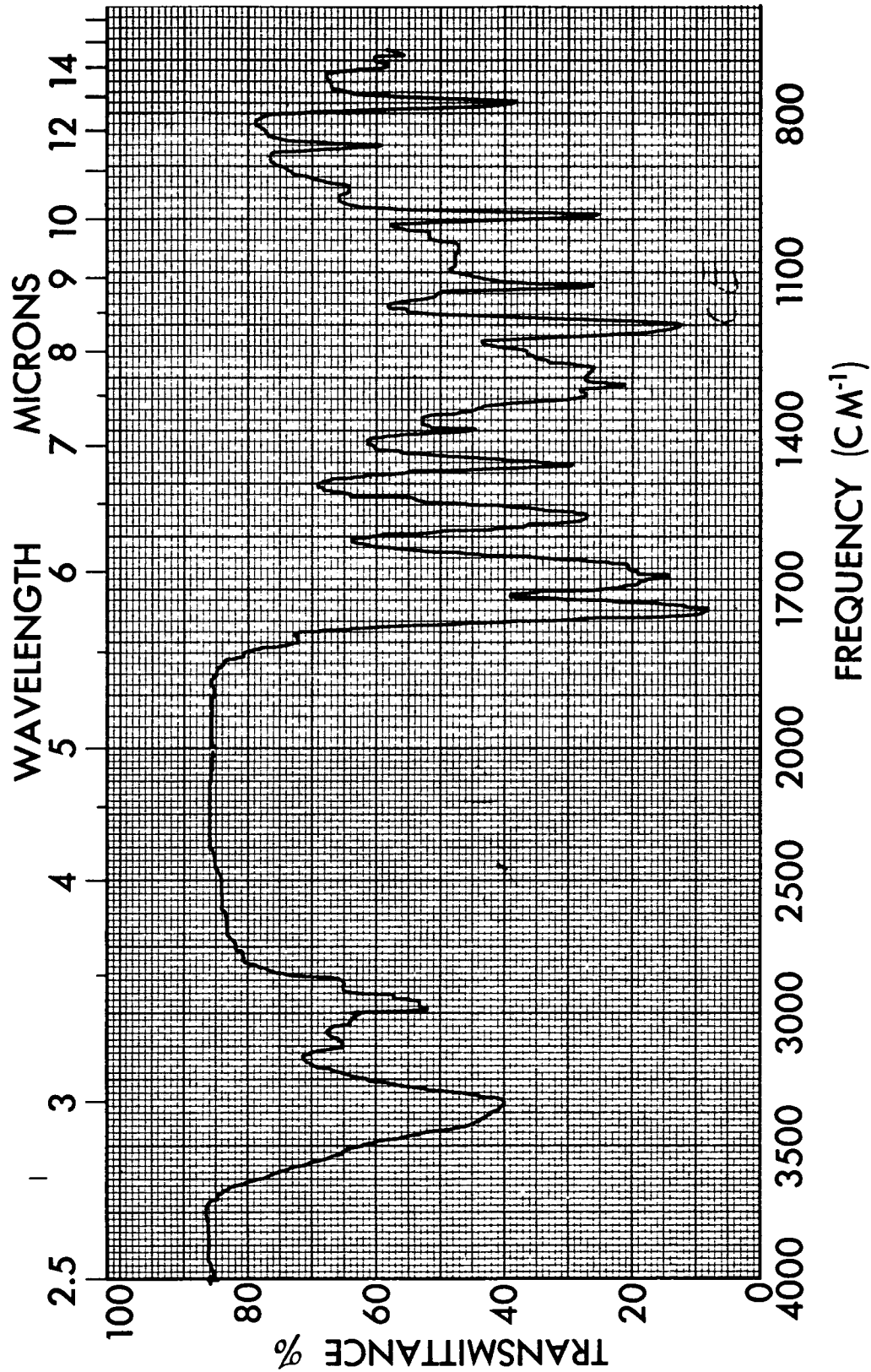


Figure 15. Infrared Spectrum of Resin C-E

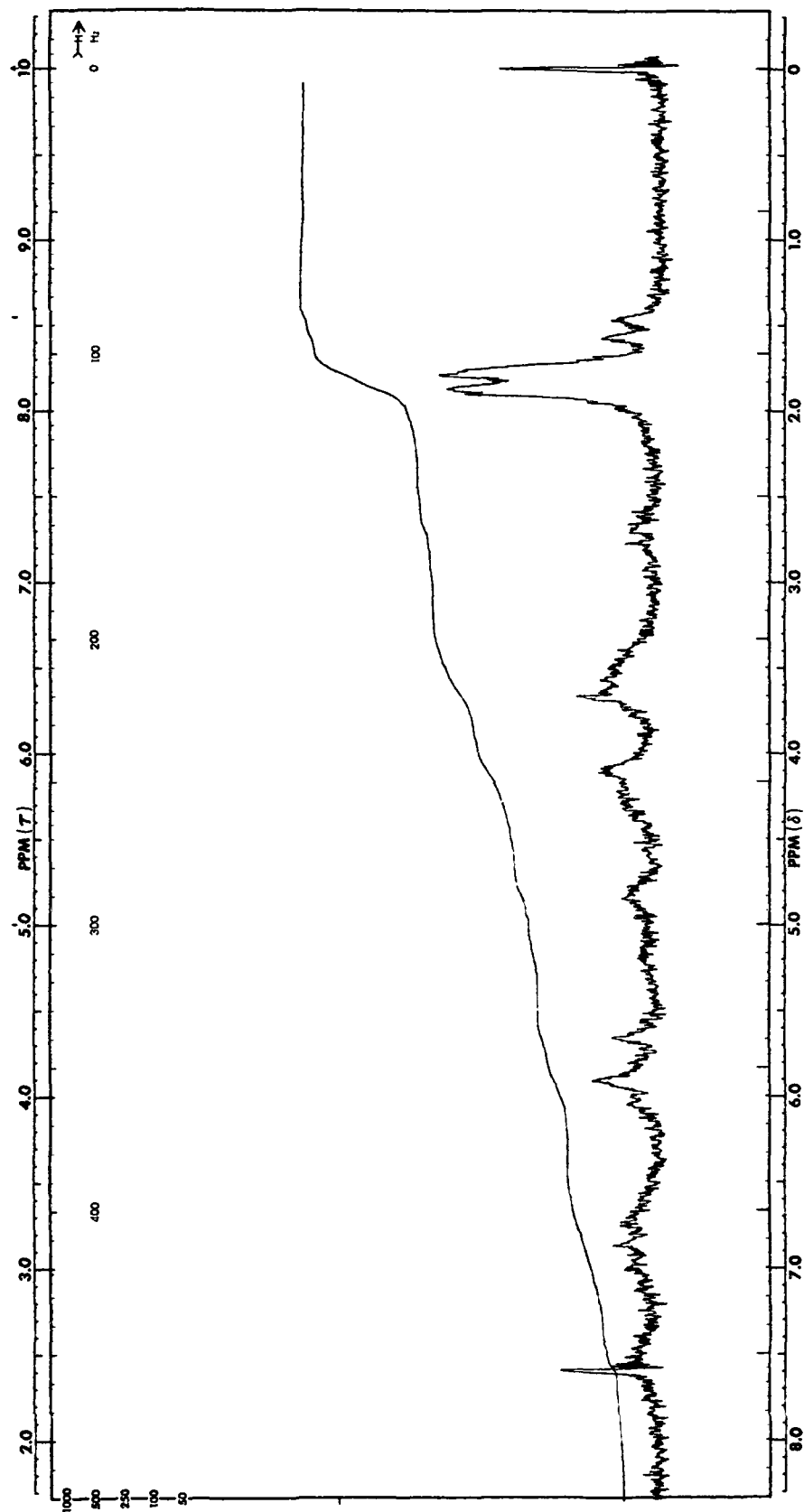


Figure 16. Nuclear Magnetic Resonance Spectrum  
of Resin C-E in CDCl<sub>3</sub>

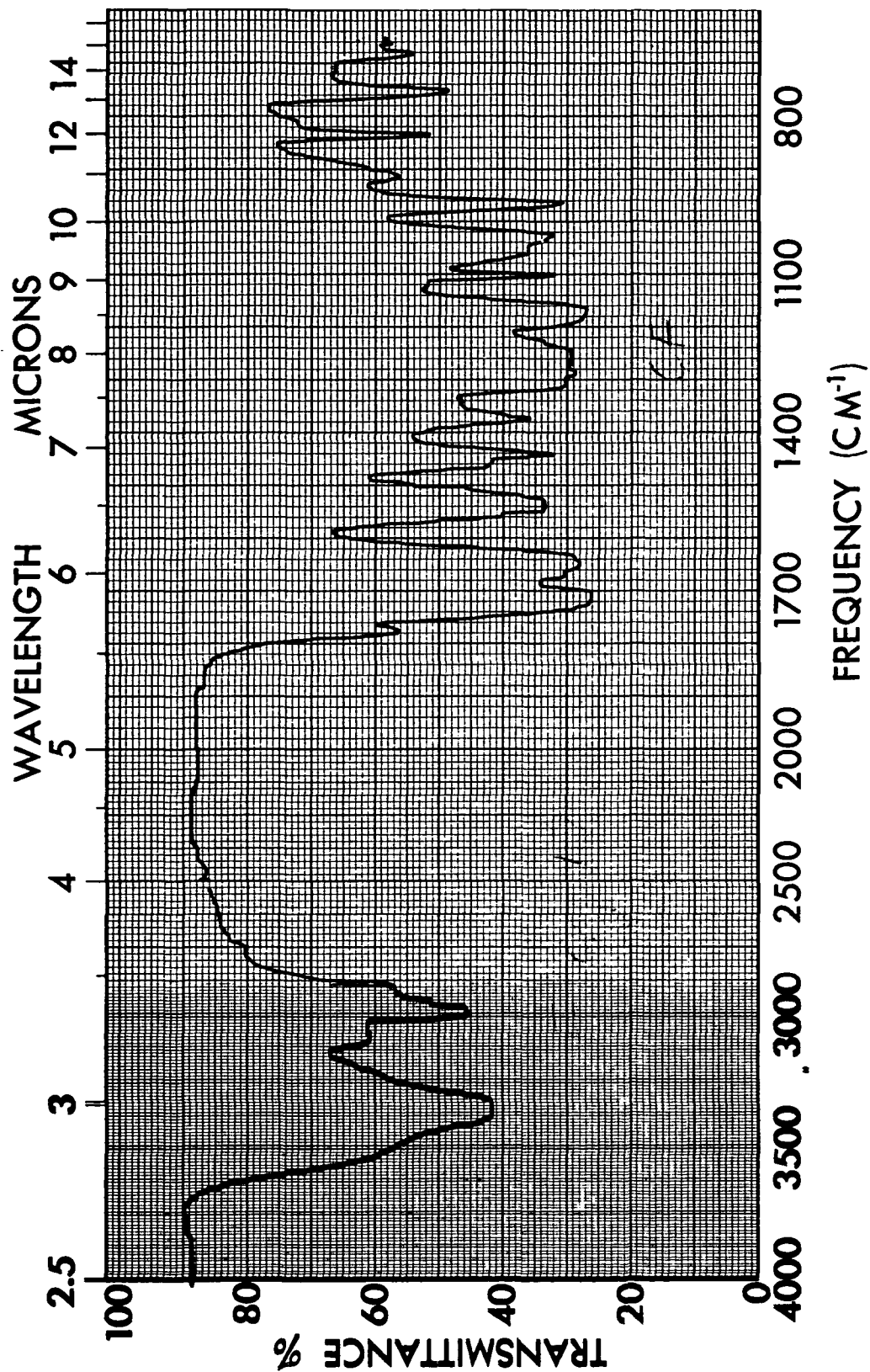


Figure 17. Infrared Spectrum of Resin C-F

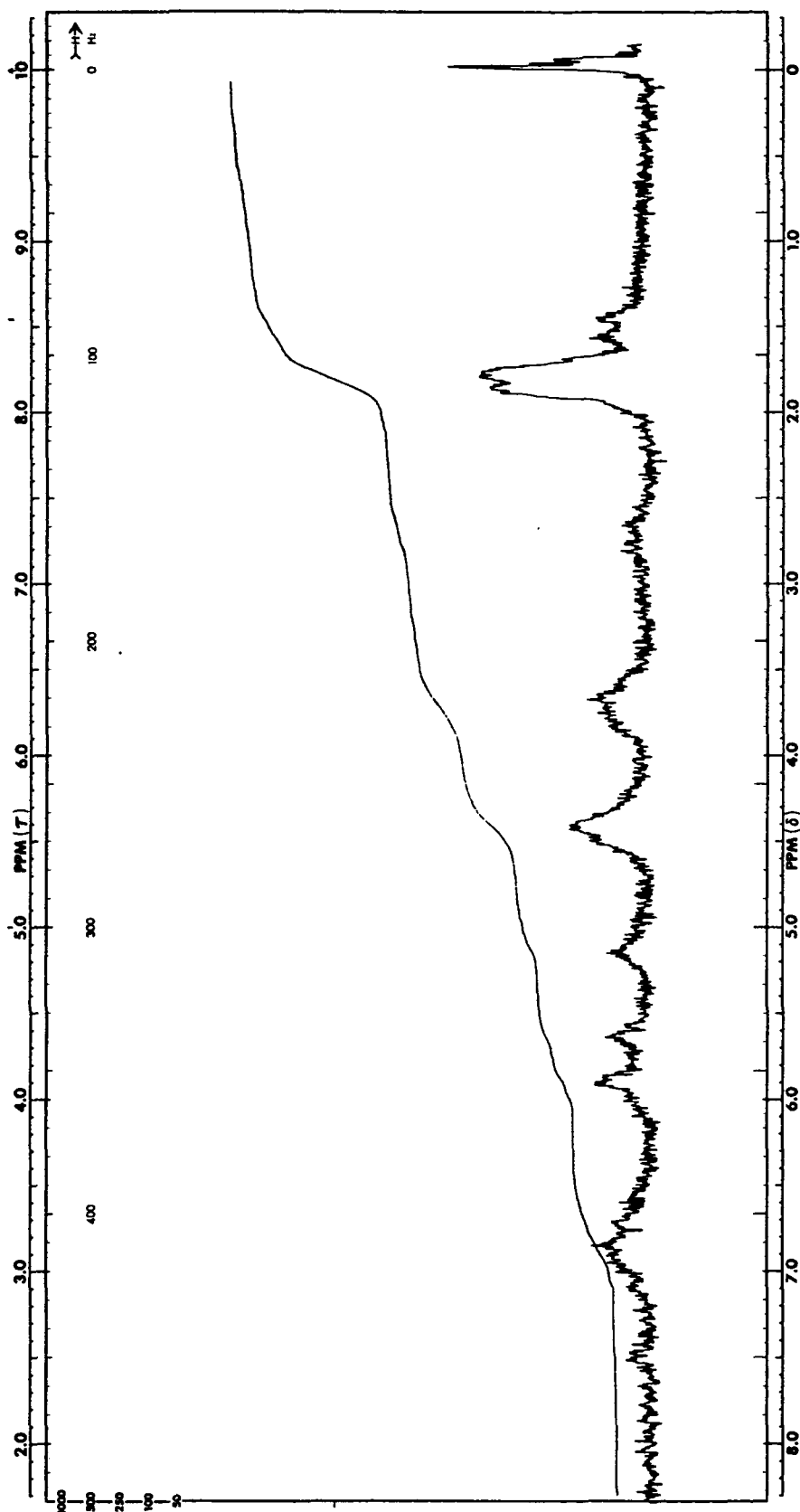


Figure 18. Nuclear Magnetic Resonance Spectrum  
of Resin C-F in  $\text{CDCl}_3$

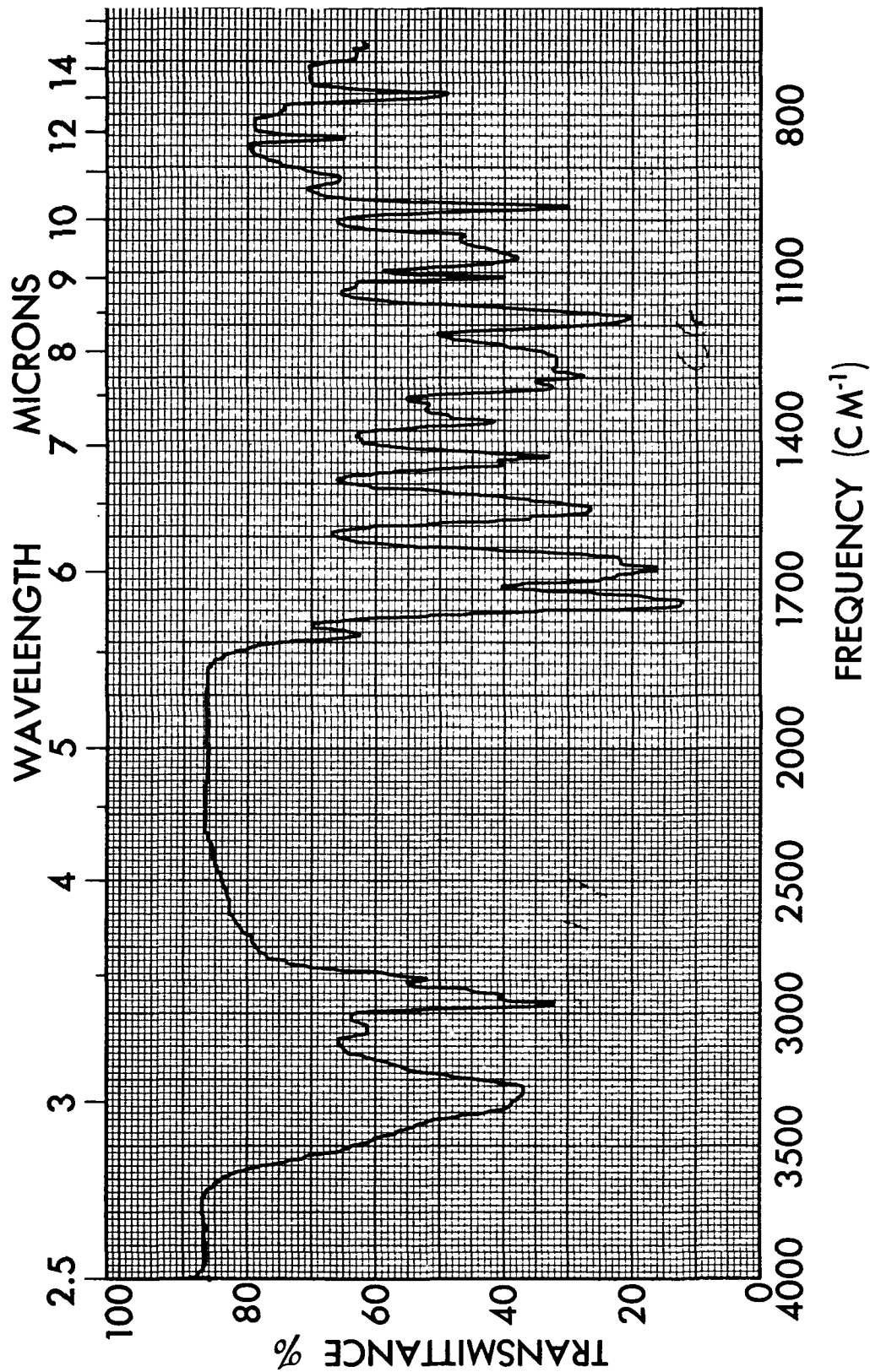


Figure 19. Infrared Spectrum of Resin C-G



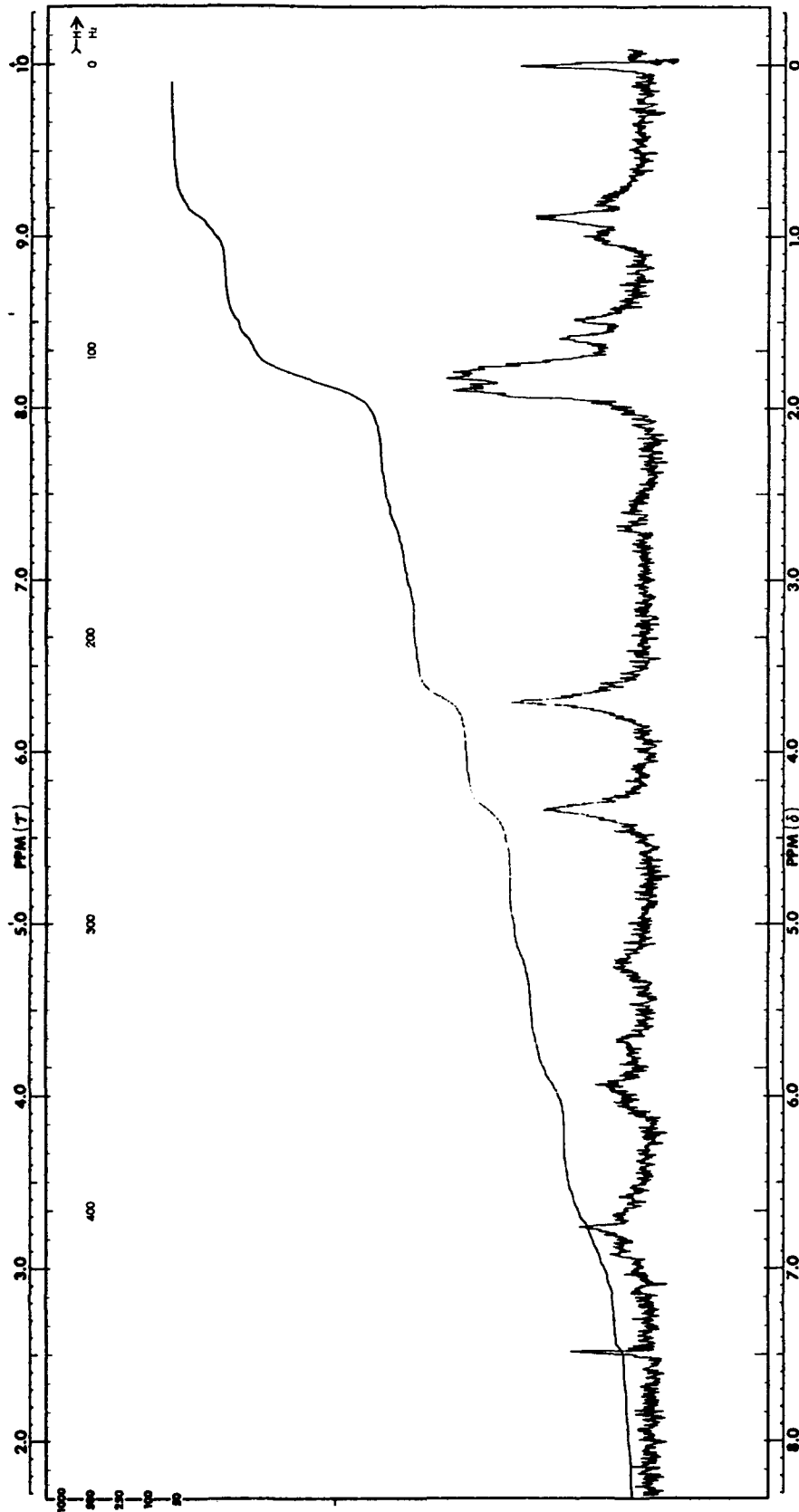


Figure 20. Nuclear Magnetic Resonance Spectrum  
of Resin C-G in CDCl<sub>3</sub>

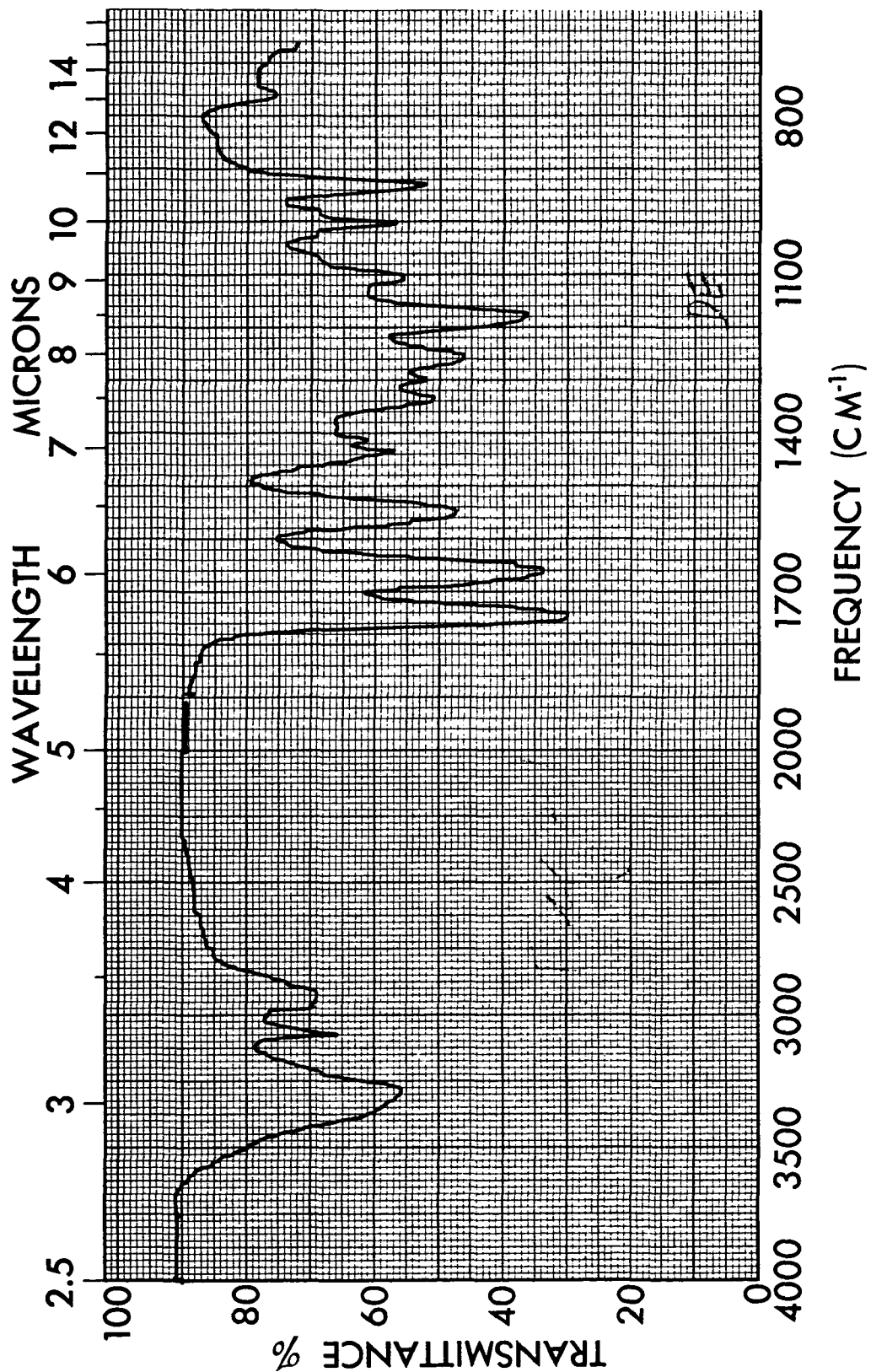


Figure 21. Infrared Spectrum of Resin D-E

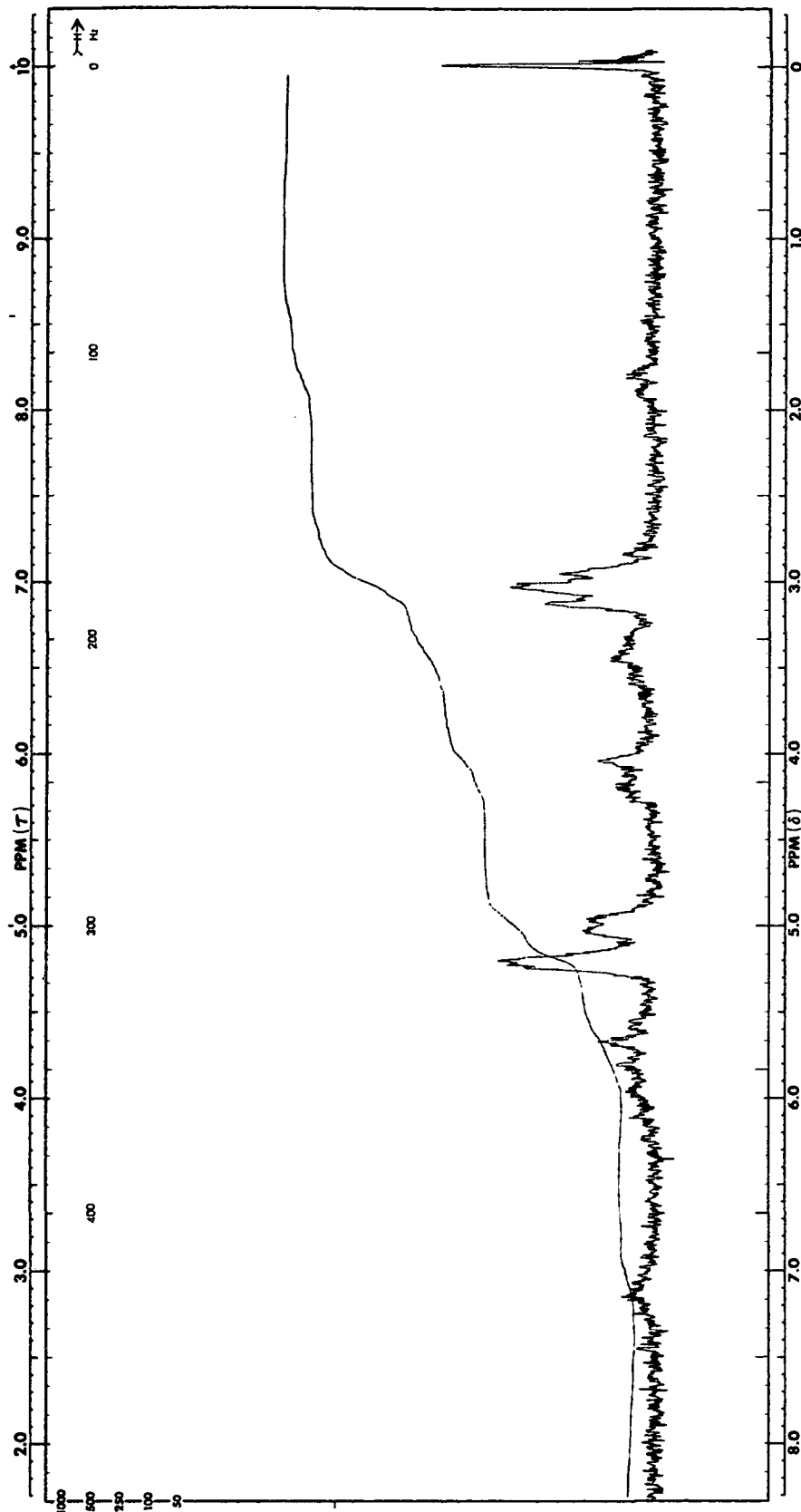


Figure 22. Nuclear Magnetic Resonance Spectrum  
of Resin D-E in CDCl<sub>3</sub>

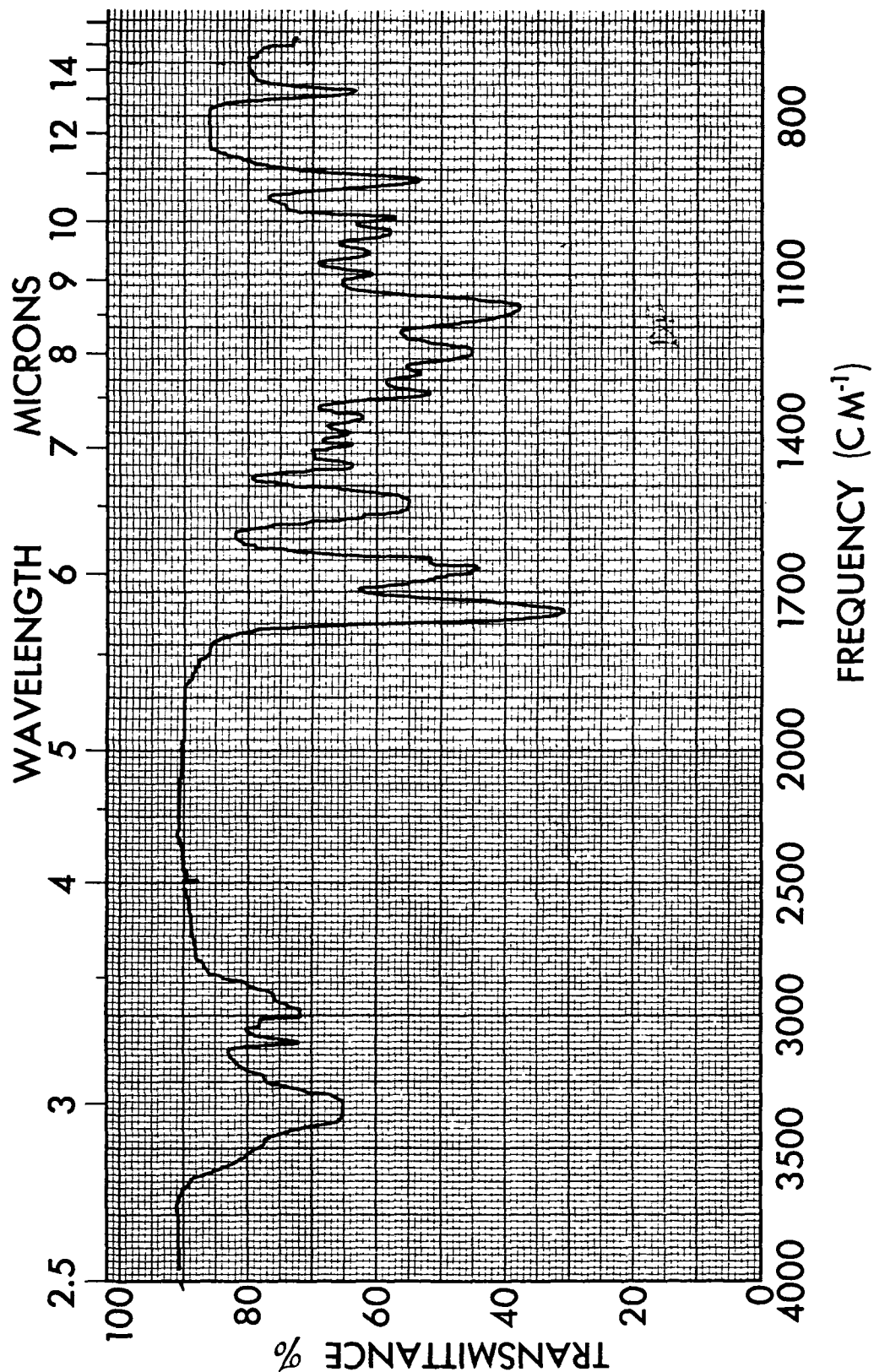


Figure 23. Infrared Spectrum of Resin D-F

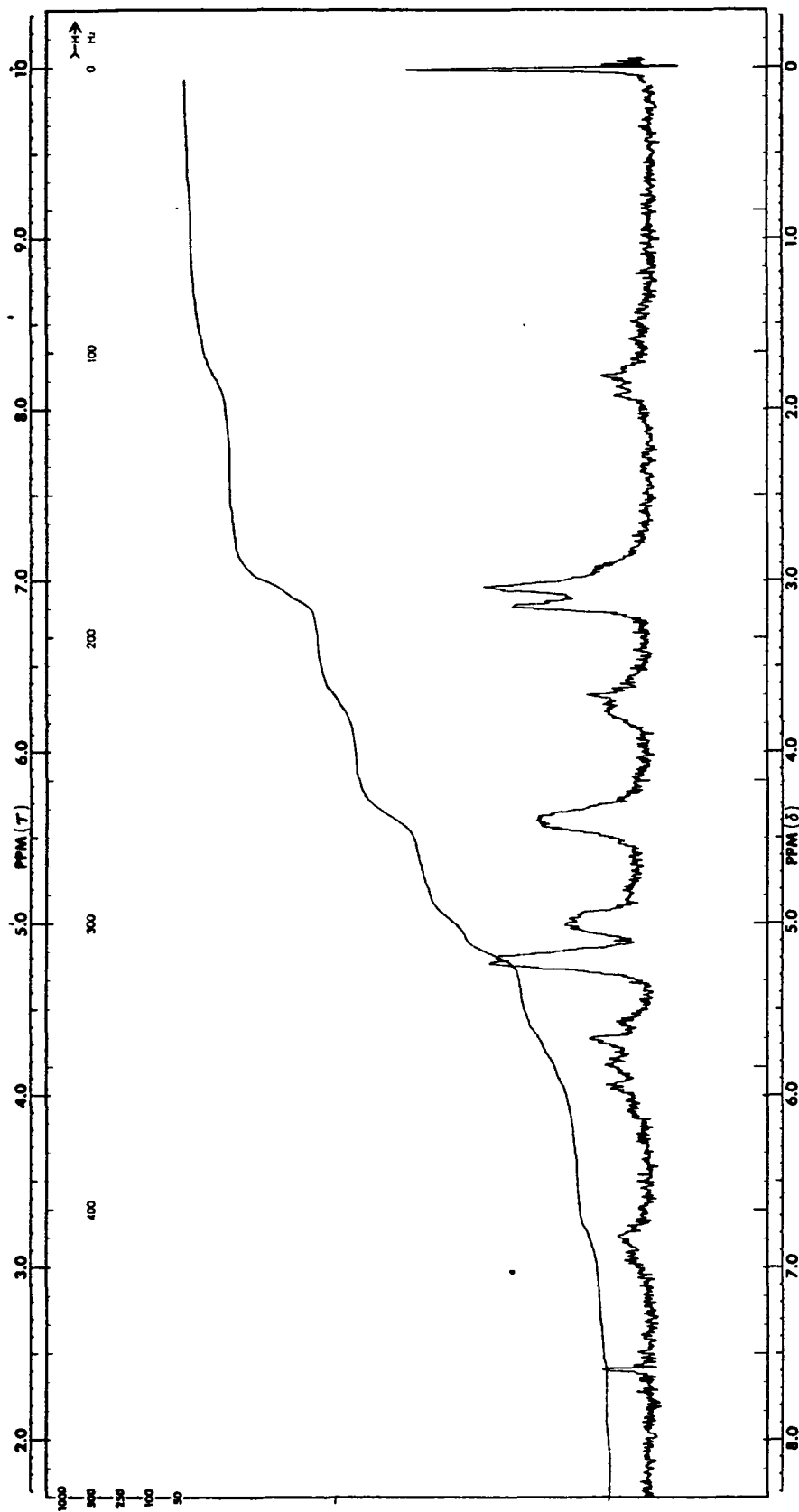


Figure 24. Nuclear Magnetic Resonance Spectrum  
of Resin D-F in  $\text{CDCl}_3$ .

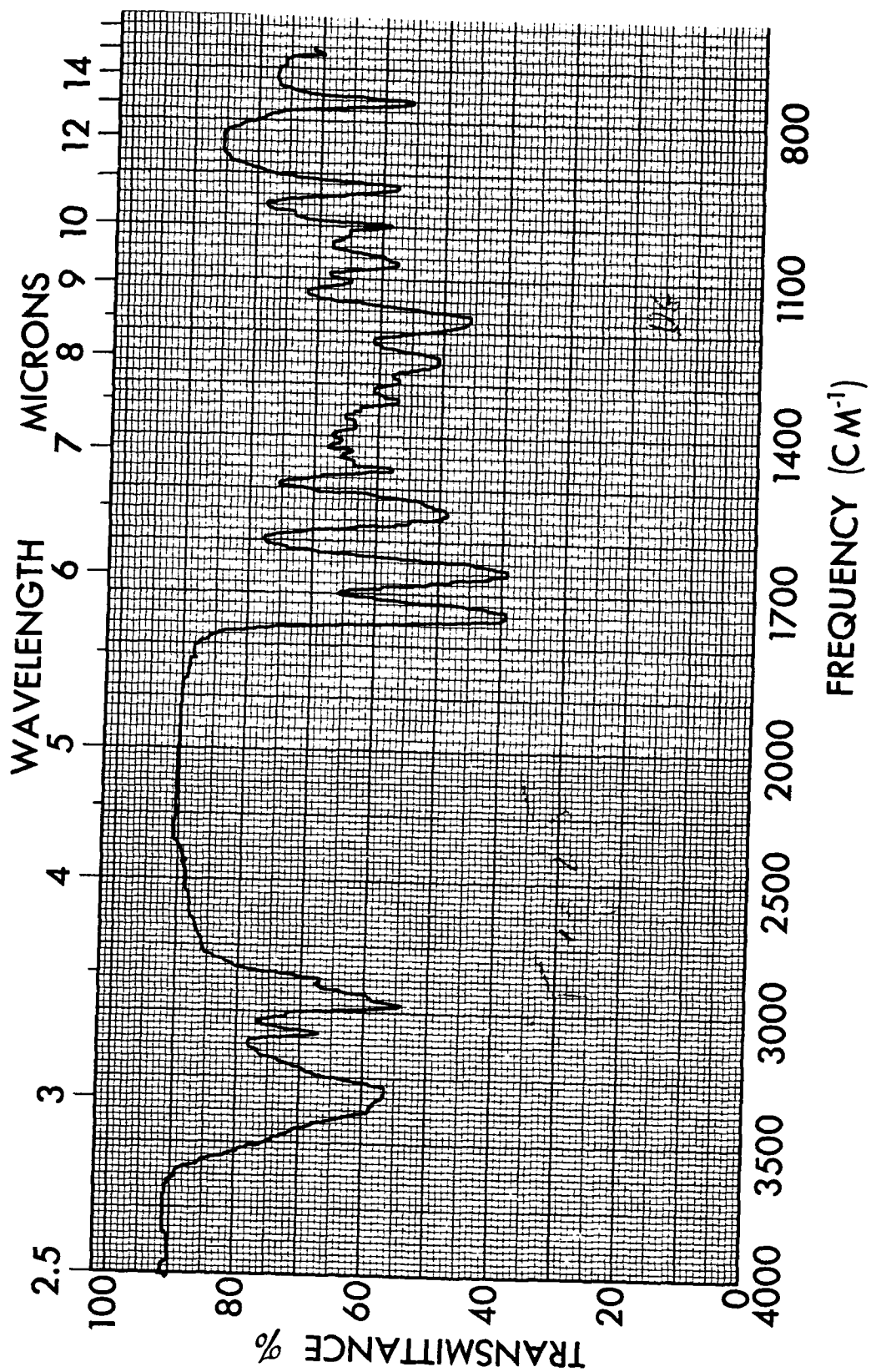


Figure 25. Infrared Spectrum of Resin D-G

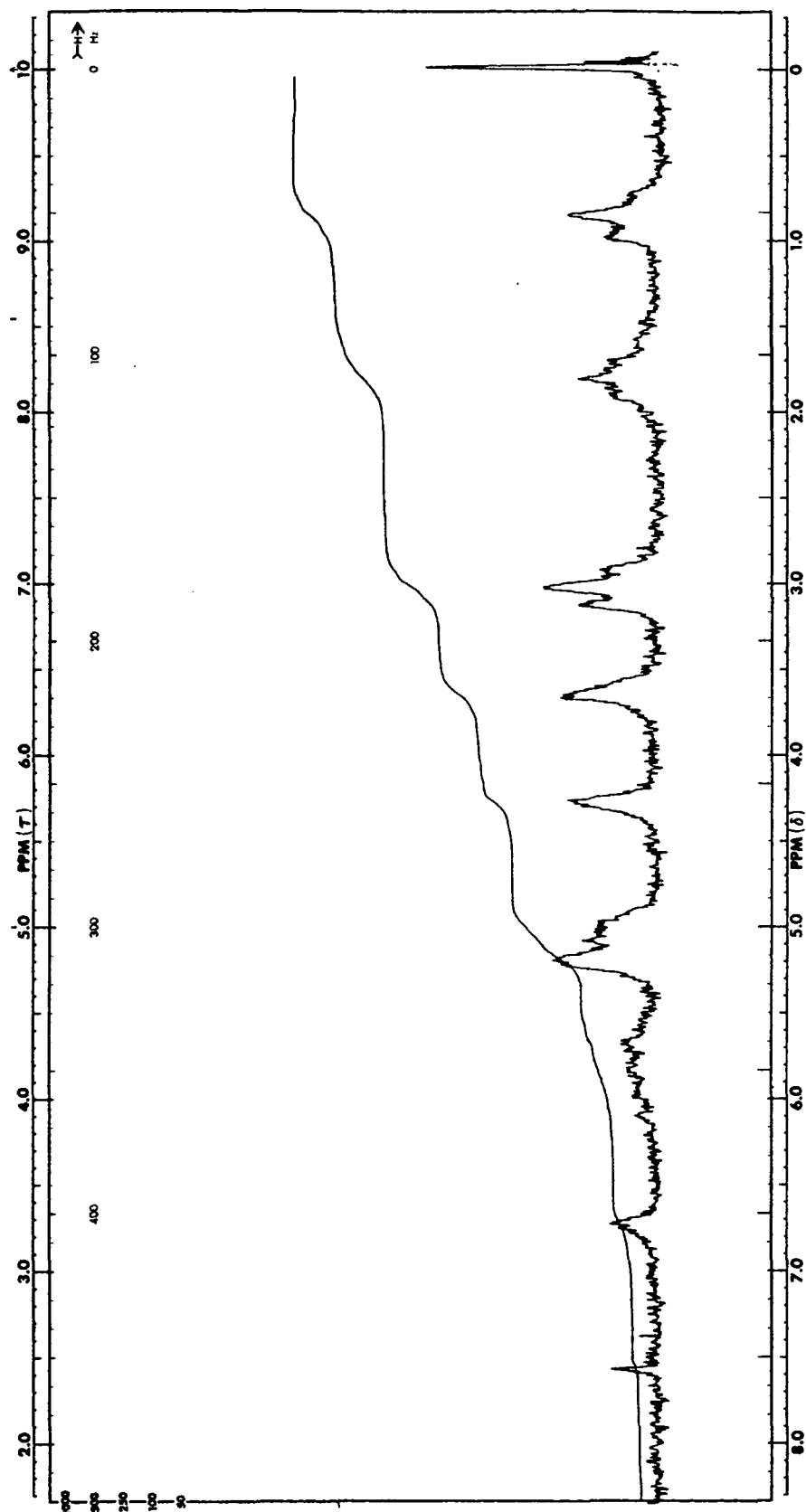


Figure 26. Nuclear Magnetic Resonance Spectrum  
of Resin D-G in  $\text{CDCl}_3$ .

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